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## Nanolithography using an Atomic Force Microscope

Alexis Gagnon Morris Centre for the Physics of Materials Department of Physics McGill University Montréal, Québec Canada

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

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Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant. To my parents, Angèle and Kevin

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## Abstract

In this thesis, I study the nanolithography of gallium arsenide samples by local oxidation with an atomic force microscope (AFM). I examine the current theoretical descriptions of the reaction kinetics and compare the results to experimental data. The main goal is to characterize the AFM oxidation process such that high quality features can be routinely patterned. I also investigate the use of alternative oxidation environments in an attempt to improve the height and aspect ratio of the AFM local oxidation features. An alternative lithography technique involving scratching under a high contact force is also studied. Finally, I discuss the steps that are necessary in order to fabricate a quantum structure with the AFM local oxidation lithography technique.

## Résumé

Dans cette oeuvre, nous avons étudié une technique lithographique basée sur l'oxydation locale de semi-conducteurs par l'entremise d'un microscope à force atomique (AFM). Nous avons débuté notre étude en résumant les idées courantes concernant le mécanisme d'oxydation par AFM. Ensuite, les prédictions des différents modèles théoriques sont mises à l'épreuve en les comparant aux données expérimentales. Notre but dans cette recherche était de caractériser le processus d'oxydation affin d'en arriver à des conclusions qui nous permettrions de prédire et de bien contrôler l'oxydation. Une forme alternative de lithographie impliquant de grandes forces de contact entre la pointe de l'AFM et l'échantillon est aussi étudiée. Finalement, nous discutons des étapes nécessaire pour former une structure quantique avec la lithographie par oxydation locale.

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# 1

## Introduction

Human beings have always been fascinated by extremes, be it tall mountains, far away galaxies, or the tiny particles that compose everything in this universe. Until recently, however, it has been difficult to study the building blocks of matter because the tools to do so did not yet exist. With the invention of the scanning tunnelling microscope (STM) in the early 1980's [1], all this changed. The STM allows one to precisely manipulate and even modify materials down to an atomic scale [2, 3, ]4]. As early as 1988, Ehrichs et al. reported successful nanopatterning of metal and semiconductor surfaces by metal deposition [5, 6]. In this experiment, a large bias voltage caused the local dissociation of an organomettalic gas and subsequent metal deposition under the influence of a large STM tip bias voltage. A few years later, a tip bias was also used by Nagahara et al. to draw 20 nm trenches on silicon and gallium arsenide under an etching solution [7]. The first report of the direct chemical modification of semiconductor surfaces in ambient atmosphere came in 1990 by Dagata and coworkers [8]. By applying a bias voltage across the STM tip and a hydrogen passivated n-Si(111) surface, they demonstrated that oxygen could be incorporated into the silicon to produce visible features that were stable even after many months of storage in air. Since this initial report, many different groups have investigated this novel STM lithography technique and confirmed that a voltage bias across the tip-sample interface produced a powerful electrical field that could locally oxidize metallic and semiconductor surfaces [9, 10, 11, 12, 13, 14].

Even though nanometer-sized features could be produced by STM local oxidation,

there were a few problems. The STM images a surface by applying a bias voltage across the tip-sample junction and measuring the resulting tunnelling current. It is the exponential dependence of this current on the tip-sample separation that makes atomic imaging possible since a slight height variation will create a large change in the current. However, in situations where the surface is affected by electrical fields, the necessity of applying a bias voltage for STMs, even during imaging is obviously problematic. Although this effect can be limited by using small imaging voltages, oxide production has been observed for bias voltages as low as 2 V [15]. Another difficulty lies with the impossibility of determining the true height of patterned oxide features since topographical and electrical information are inherently entangled when using the STM.

Fortunately, an alternative scanning probe technique invented a few years after the STM solved these problems. Instead of using tunnelling current as a feedback signal, the atomic force microscope (AFM) measures the contact force between the sample surface and a sharp tip by using a flexible cantilever [16]. By de-convoluting the imaging and lithography mechanisms, it was now possible to directly observe the lithography pattern without fear of accidental surface modification during the imaging process. Even insulating substrates no longer posed any problems since the AFM-feedback mechanism doesn't depend on electrical interactions. Day and coworkers were the first to realize the advantages of using an AFM over an STM for the purpose of lithography by local oxidation [17]. Since, research into this technique has proliferated, with a large number of groups reporting success for both contact [18, 19, 20, 21, 22, 23] and non-contact [24, 25] AFM operational modes <sup>1</sup>. Despite the differences between STMs and AFMs, the oxidation process itself is fundamentally the same, and is often simply referred to as scanning *probe* microscope (SPM) local oxidation.

In the last few years, the combination of SPM local oxidation with shallow two-<sup>1</sup>The various AFM imaging techniques will be discussed in chapter 3.

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dimensional electron gases (2DEG) embedded in GaAs/AlGaAs heterostructures has generated considerable excitement. In 1995, Ischii and coworkers observed that drawing a series of oxide lines across the heterostructure cap layer resulted in an increase in the 2DEG resistance beneath the oxide [26], while further work by Held *et al.* confirmed that, under the right conditions, shallow 2DEGs could be completely depleted by the SPM oxide [27, 28, 29]. These results have had profound implications, indicating that it was now possible to pattern substantially smaller tunable quantum devices with SPM oxidation than was previously possible with conventional optical and electron beam lithography techniques.

While SPM oxidation holds great promise as a lithography technique, it does not come without any of its own problems. The depletion of embedded 2DEGs occurs mainly because the SPM oxide acts as a highly localized etch of the cap layer of the GaAs/AlGaAs heterostructure. Numerical simulations have shown that the band diagrams of these heterostructures are very sensitive to the thickness of the GaAs cap layer. Indeed, Heinzel *et al.* have shown that the electron density within a 40 nm deep 2DEG will be completely drained if a thickness of at least 8 nm of this cap layer is either removed or oxidized [30]. However, once the depth of the 2DEG is increased, the SPM oxide no longer acts as an effective barrier: even the current maximum achievable oxide depth of 15 nm fails to deplete a 2DEG situated 80 nm beneath the surface [31]. Here lies the main problem of this lithography technique. Although some progress has been made [32], it is currently very difficult to produce high quality 2DEGs close to the sample surface. A proper understanding of the oxidation mechanism and of the oxide properties is therefore critical to extend oxide growth deeper into heterostructure surfaces and produce high-quality electronic devices.

In the literature, most reports have concentrated on the SPM oxidation of Si while surprisingly few, considering the importance of the GaAs/AlGaAs heterostructures, have examined GaAs. The work presented in this thesis has focused on the characterization of lithography by SPM local oxidation on GaAs substrates. It is organized as follows. After this introduction, existing theoretical models of the oxidation process are reviewed in chapter 2. In chapter 3, I describe the AFM and the experimental setup. In chapter 4, I discuss the main experimental results dealing with the influence of oxidation parameters such as tip voltage, writing speed and environment on SPM oxides. Next, in chapter 5, substrate scratching using the AFM tip is presented as an alternative lithography technique that could be used in conjunction with local oxidation. In chapter 6, I discuss attempts at creating a quantum device with the AFM lithography technique. Finally, I conclude in chapter 7 with a review and outlook on the future applications of this work.

## SPM Oxidation Theory

Currently two mechanisms are thought to be at work in SPM local oxidation: anodization of the adsorbed water layer [33, 34] and field-enhanced diffusion of ionic species [23]. The tip-surface interface can be thought of as being a nanometer-sized electrolytic cell. In a typical anodic oxidation reaction, a material is immersed in an electrolytic solution and biased anodically (positively) with respect to a counter electrode, providing the necessary energy for the oxidation reaction to proceed. In the case of SPM oxidation, an adsorbed water layer acts as the electrolyte while the potential difference is applied across the tip and sample. Because of the small distance across which the potential is applied, enormous electrical fields in excess of  $10^9$  V/m can be produced that drive the oxidizing agents across the growing oxide layer, enhancing the oxidation process.

In 1949, Cabrera and Mott proposed a field-enhanced mechanism for the low temperature oxidation of metals [35]. It had been experimentally observed that many metals that readily oxidized at high temperatures would, at lower temperatures, experience limited oxide growth. This self-limiting behaviour is also present in SPM local oxidation and so many groups have turned towards the Cabrera and Mott formalism looking for a theoretical description of the SPM results. However, we shall see that even though some of Cabrera and Mott's predictions are correct, others, concerning the kinetics of the SPM local oxidation reaction, are not. One of the main problems in the Cabrera and Mott formalism is that it doesn't account for the action of important effects such as space charge accumulation within the growing oxide. Consequently, in the last few years considerable effort has been invested to incorporate these effects into a consistent description of SPM local oxidation. Unfortunately, agreement in the scientific community about the form of such a model has not yet been reached. Because of its importance, I will begin this chapter by a review of the Cabrera and Mott model, after which alternative propositions will be examined. Comparisons with experimental results will be made in chapter 4.

#### 2.1 Cabrera and Mott

The Cabrera and Mott model is based upon a consideration of the diffusion of ionic species through the oxide layer. Cabrera and Mott begin by hypothesizing that an intense electrical field is formed across the oxide film due to the contact potential between adsorbed oxygen and the metal surface. Because of the presence of this field, ionic species are able to diffuse through the oxide and continue the oxidation reaction, even at low temperatures where it would otherwise cease. But, since the electrical field depends on the oxide thickness (E = V/h), the oxide will eventually reach a limit where the field is too weak to enhance the ionic diffusion and the growth will stop. When applying this analysis to SPM oxidation, it is oxygen species that diffuse instead of the metal ions, while the driving field is created by the SPM tip voltage.

In order to diffuse from one interstitial site to the next, an ion has to overcome a potential barrier U. In the absence of an external field, the probability per unit time that an ion will move forward is  $\nu \exp(-U/kT)$ . In the Cabrera and Mott model we are dealing with positively charged ions, so the action of an electrical field is to lower the potential barrier U by  $\frac{1}{2}qaE$  for diffusion in the direction of the field, where q is the ionic charge and a is the distance between interstitial sites. Similarly, the barrier is raised by the same amount in the opposite direction. The probability of moving forwards is then proportional to the difference between the forward and backward probabilities, hence

$$p = \nu \left[ \exp \left( -U/kT + \frac{1}{2}qaE/kT \right) - \exp \left( -U/kT - \frac{1}{2}qaE/kT \right) \right]$$

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$$= \nu \exp\left(-U/kT\right) \left[ \exp\left(\frac{1}{2}qaE/kT\right) - \exp\left(-\frac{1}{2}qaE/kT\right) \right]$$
$$= 2\nu \exp\left(-U/kT\right) \sinh\left(\frac{1}{2}qaE/kT\right).$$
(2.1)

In the higher temperature ranges, metallic oxide thicknesses are large enough so that  $E = V/h \rightarrow 0$  and thus  $p \propto E$  since for small x,  $\sinh(x) \simeq x$ . However, for very thin films, as is the case for SPM oxides, the electrical field can be very large and therefore this approximation is no longer valid. In these cases,  $exp\left(-\frac{1}{2}qaE/kT\right) \rightarrow 0$  and the probability assumes an exponential dependence on the field:

$$p \simeq \nu \exp\left(-U/kT\right) \exp\left(\frac{1}{2}qaE/kT\right).$$

To calculate the oxide growth rate, the parameters N, the number of ions per unit area, and  $\Omega$ , the volume of oxide per metal ion, are introduced. The growth rate is then simply a multiplication of these parameters with the probability

$$\frac{\mathrm{d}h}{\mathrm{d}t} = N\Omega\nu\exp\left(-U/kT\right)\exp\left(\frac{1}{2}qaE/kT\right).$$

By substituting E = V/h and by defining  $u \equiv u_0 \exp(-U/kT)$ ,  $u_0 \equiv N\Omega v$  and  $h_0 \equiv \frac{1}{2}qaV/kT$ , the growth is then recast into the simple form

$$\frac{\mathrm{d}h}{\mathrm{d}t} = u \exp\left(h_0/h\right). \tag{2.2}$$

For SPM oxidation, h and  $h_0$  are respectively on the order nanometers and tens of nanometers [36], hence an approximate solution for h(t) is found by integrating by parts and dropping all higher order terms in  $h/h_0$ . The solution is

$$ut = (h^2/h_0) \exp(-h_0/h)$$
. (2.3)

At this point, Cabrera and Mott introduce a thickness  $h_L$  corresponding to the maximum oxide height after which growth has stopped. In 1997, Stiévenard *et al.* adapted the Cabrera and Mott model to SPM oxidation [36] and defined  $h_L$  as

$$h_L = V/E_L,$$

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where  $E_L$  is the minimum field for which the SPM oxidation reaction takes place. For  $h \ll h_0$ , Stiévenard approximated Eq. 2.3 by

$$\frac{1}{h(t)} = \frac{1}{h_0} \ln\left(\frac{h_L^2}{h_0 u t}\right).$$
 (2.4)

This is the so-called inverse logarithmic kinetic equation relating oxide height to voltage pulse duration. It is important to realize that the electrical potential V contained within the  $h_L$  constant isn't limited to the contact potential between adsorbed oxygen species and metal surfaces; instead V represents the action of any external electrical potential. In the case of SPM anodic oxidation, V represents the bias voltage applied between the tip-surface junction.

To further adapt Eq. 2.4 to SPM oxidation, the oxidation time t is replaced by W/v where W is the oxide width and v the SPM tip velocity. The relationship then becomes

$$\frac{1}{h} = \frac{1}{h_0} \ln(v) + \frac{1}{h_0} \ln\left(\frac{h_L^2}{h_0 u W}\right),$$
(2.5)

or, recast into a simpler form,

$$\frac{1}{h} = \frac{1}{h_0} \ln\left(\frac{v}{v_0}\right) \tag{2.6}$$

where  $v_0 = h_0 u W / h_L^2$ . For an expression relating height to voltage, v is set as constant in Eq. 2.5, and remembering that  $h_0 = q a V / kT$ ,

$$h = \frac{kT/qa}{\ln\left(h_L^2 v kT/qa u W\right) - \ln V} V$$

If  $\ln(h_L^2 v kT/qauW) \gg \ln V$ , this relation is linear with V:

$$h \simeq \frac{kT/qa}{\ln\left(h_L^2 v k T/q a u W\right)} V. \tag{2.7}$$

This is a reasonable assumption since  $\ln(h_L^2 v k T/q a u W)$  is on the order of 20–25 [36] and typical bias voltages in SPM oxidation are less than 30V, thus  $\ln(V) \leq 3.4$ .

As we will see in chapter 4, the Cabrera and Mott formalism correctly describes the linear relation between oxide height and voltage present in my data. On the other hand, things aren't as clear with the inverse-log time dependence. Starting with Avouris *et al.* in 1997 [37], many groups have favored a direct-log form. As pointed out by Dubois and Bubendorff [38], the inverse-log solution isn't mathematically consistent with the original rate equation (Eq. 2.2), which is can be seen by substituting the solution Eq. 2.4 into Eq. 2.2 giving  $dh/dt = uh_L^2/h_0 ut$ . Solving this leads to the direct logarithmic solution  $h(t) = k'(V) \log(t)$ . It is then surprising that, despite this problem, the Cabrera and Mott formalism correctly predicts the linear relationship between bias voltage and oxide height that has been consistently observed for SPM oxidation of Si [19, 22, 39, 40, 41], Si<sub>3</sub>N<sub>4</sub> [42], GaAs [43, 44, 45], InGaP [45], InGaAs [46] and even amorphous Si [47].

### 2.2 The Effect of Space Charge

The electrical field plays a major part in the Cabrera and Mott formalism—we have showed that, without the presence of this field, low-temperature ionic diffusion, and consequently oxidation, is impossible. From this it follows that any modification to this field could have important consequences on the oxidation rate. Recently, experimental evidence has been brought forth to indicate that an accumulation of space charge within the growing oxide, and its effect on the electrical field E, may actually be the limiting factor in SPM oxide growth [48, 49, 50, 51]. However, no consensus exists on the origin of this space charge. For example, in Ref. [48], Dagata and coworkers used a non-contact electrical force measurement technique called Scanning Maxwell-Stress Microscopy (SMM)<sup>1</sup> to investigate the variation in surface potential and capacitance during SPM oxide growth in Si. Their results showed an accumulation of positive charges which they interpreted to be H<sup>+</sup> ions produced during the oxidation reaction Si +  $4h^+$  +  $2OH^- \longrightarrow SiO_2 + 2H^+$ . On the other hand, using spatially resolved photoemission spectroscopy [55, 56], Lazzarino *et al.* [51] came to the conclusion that positive charges are produced only on the SiO<sub>2</sub> surface through a

<sup>&</sup>lt;sup>1</sup>For complete description of SMM see Refs. [52, 53, 54]

local photoemission process, and thus dismissed the charge trapping model proposed by Dagata *et al.* in Ref. [48]. Regardless of the source of this space charge, there *is* agreement amongst the scientific community that a complete model of the SPM oxidation process should include space charge effects.

At the time of writing of this thesis, there are three main theoretical descriptions of the SPM oxidation process, each having different predictions regarding the oxidation kinetics. The first model, by Stiévenard *et al.*, has already been presented above and was quite simplistic in the fact that space charge effects were omitted. The remaining two theories stem from the inclusion of space charges and will now be discussed.

#### 2.3 Power Law Kinetics

In 1989, Wolters and Zegers-van Duynhoven [57] showed that the traditionally accepted high temperature linear-parabolic description of dry silicon oxidation,

$$t = \tau + (A/B)h + (1/B)h^2,$$

was actually an approximation of a power-of-time law,  $t = Ah^{\alpha}$ . To derive the power law, Wolters and Zegers-van Duynhoven proceeded in manner very similar to that of Cabrera and Mott by considering the ionic transport through the growing oxide in the presence of an electrical field. However, their approach differed by the inclusion of space-charge effects. Wolters and Zegers-van Duynhoven proposed that positive charges would accumulate close to the oxide-silicon interface due to defects in the oxide structure created by a high oxide growth rate. Even though SPM oxidation conditions are very different than standard thermal oxidation, an empirical power law proposed by Teuschler *et al.* [22] and then Ley *et al.* [39] provided a surprisingly good fit to a wide range of experimental data:

$$h(t) = \alpha (V - V_0) (t/t_0)^{\gamma}.$$
(2.8)

In this model,  $\alpha$  and  $\gamma$  are parameters,  $t_0$  is an arbitrary constant, and  $V_0$  is the threshold voltage. However, this relation was purely empirical and no theoretical

basis was given to provide insight into its physical meaning. The success of the Teuschler model led Dubois and Bubendorff to successfully adapt [38] Wolters and Zegers-van Duynhoven's model to SPM oxidation. Without going into too many details, the main points of Dubois and Budendorff's theory are presented below.

First, the number of trapped charges per unit area is calculated. By considering Coulomb interactions between trapped and newly incorporated charges, this density N is found to be:

$$N = \frac{1}{s} \ln \left( 1 + \frac{Q}{Q_0} \right), \tag{2.9}$$

where s is the area occupied by a trap and  $N_0$  is the maximum areal trap density. Now, the presence of a large concentration of these trapped charges will have a considerable effect on the initial electrical field applied across the oxide film. Dubois and Bubendorff argue [38] that the trapped charges are confined close to the bulk-oxide interface, at a distance  $h_0$ , since most of the charge defects originate from an incomplete saturation of broken silicon bonds. Because of this, the electrical field is reduced by the amount

$$E = E - \frac{qN}{\epsilon} \frac{h - h_0}{h}.$$
(2.10)

This new electrical field is then inserted into the Cabrera and Mott's general ionictransport equation,

$$\frac{\mathrm{d}h}{\mathrm{d}t} = u_0 \exp\left(-U/kT\right) \sinh\left(\frac{1}{2}qaE/kT\right),\tag{2.11}$$

and after a few simplifications the following rate equation is found (for details, see Ref. [38]):

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \left[u_0 \exp\left(-U/kT\right) \exp\left(\frac{h_a}{h}\right)\right] \left(\frac{h}{h_b}\right)^{-\delta},\qquad(2.12)$$

where  $h_a$  and  $h_b$  are constants, with  $h_a \propto V$ . To integrate Eq. 2.12, Dubois and Bubendorff assume that  $\delta$  is an integer. Although this assumption was made purely to simplify the integration and obtain a tractable relation between h and t, Dubois and Bubendorff argue that this isn't too severe a limitation since they find that for

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SPM oxidation experimental conditions,  $\delta$  usually varies between 2–6. With this simplification, an approximate solution of Eq. 2.12 is found:

$$h = h_b \left(\frac{t}{t_0}\right)^{1/(\delta+1)} = h_b \left(\frac{t}{t_0}\right)^{\gamma}, \qquad (2.13)$$

where  $t_0$  is a voltage-dependent time constant.

Power law kinetics have been observed by many different groups. In their experiments on Si(111) from which Eq. 2.8 was deduced, Teuschler *et al.* have shown that  $\gamma$  does not depend on substrate doping—in all cases  $\gamma = 1/4$  [22, 39]. A Different exponent of  $\gamma = 1/2$  has been reported by Hattori *et al.* for Si(111) [19] and Yasutake *et al.* for Si(100) [18], while Dubois and Bubendorff obtained  $\gamma = 1/5$  for TiO<sub>2</sub>. Unfortunately, the power-law derived by Dubois and Bubendorff does not show  $h \propto V$ , as did Teuschler's empirical equation (Eq. 2.8), or Stiévenard's adaption of Cabrera and Mott (Eq. 2.7).

#### 2.4 Direct Logarithmic Form

In 1997, Avouris et al. proposed a direct logarithmic form,

$$h(t) = k(V)\ln(t),$$
 (2.14)

which was obtained based on experiments made with Si(100) [15, 37]. According to the Cabrera and Mott model, the oxide growth rate, dh/dt, has an exponential dependence on electrical field, but experimental results by Avouris *et al.* indicated otherwise. To account for the larger than expected variations in oxidation rate, an increase of the activation energy due stress coming from the density mismatch between Si and SiO<sub>2</sub> was proposed. However, this stress mechanism was later refuted by Dagata *et al.* on the basis that the associated activation energy and decay length were more descriptive of high-temperature thermal oxidation. Nevertheless, there are many reports of direct-log kinetics for SPM oxidation throughout the literature for various types of materials such as GaAs [44, 58, 59] and Si [60, 61] indicating that more investigation into the direct-log form was warranted.

#### 2: SPM Oxidation Theory

At the time Cabrera and Mott published their inverse-log kinetic equation, both it and direct-log forms had been experimentally observed but sufficient evidence to determine which was correct did not yet exist. In time though, it was the direct-log form that emerged victorious [62, 63, 64], prompting Herbert Uhlig to publish in 1956 a theoretical derivation of the direct-log relation for the low-temperature oxidation of metals [65]. To obtain the direct log form, Uhlig considered that the rate-limiting process in oxide formation was actually the diffusion of electronic species (instead of metal ions, like it was for Cabrera and Mott). Supposing that this is indeed the case, the oxidation rate will then be directly proportional to the current I flowing through the oxide-metal junction. For low temperatures, this current follows a relation of the form [66]

$$I = A' \exp\left[\frac{-e(\phi - V)}{kT}\right]$$
(2.15)

where A is a constant,  $\phi$  is the work function of the metal and V is the electrical potential across the metal-oxide interface. Consequently

$$\frac{\mathrm{d}h}{\mathrm{d}t} = A \exp\left[\frac{-e(\phi - V)}{kT}\right],\tag{2.16}$$

where in the Cabrera and Mott theory, V was the contact potential between adsorbed oxygen and the metal surface. With Uhlig however, V is the potential created at the metal-oxide interface due to an accumulation of space charge within the growing oxide.

When a metal is in contact with an oxide having a greater electron affinity, the oxide will accumulate excess negative charge while an equal amount of positive charge flows into the metal. When the field created by this electrical double layer compensates exactly for the difference in work functions, charge transfer will stop. Since metals have an abundance of mobile charge carriers, the double layer is confined to a very small area at the interface. For semiconducting oxides however, very few electrons can be excited into the conduction band and the excess charges are instead trapped in a limited number of lattice imperfections and defects, extending the reach of space charge deep into the oxide. Consequently, as the oxide grows, so will the total amount of trapped negative space charge.

To calculate V, Uhlig integrates the Poisson equation

$$\frac{\mathrm{d}^2 V}{\mathrm{d}y^2} = \frac{4\pi ne}{\epsilon},\tag{2.17}$$

where n is the density of trapped electrons, and  $\epsilon$  is the oxide dielectric constant. From there, the results are inserted into Eq. 2.16 and integration of this oxide growth rate equation gives the logarithmic law

$$h = k_0 \ln\left(\frac{t}{\tau} + 1\right) \tag{2.18}$$

which is very similar to the empirical Avouris direct log form (Eq. 2.14).

In 2000, Dagata et al. [67] recognized the parallels that existed between their experimental observations of space charge accumulation within the growing SPM oxide and Uhlig's theory. While in Dagata's case accumulation of positive instead of negative charge was recorded, Uhlig's direct log form seemed to apply very well to published experimental SPM results. However, the many reports that showed the Teuschler power law working just as well were quite troubling. Dagata et al. overcame these problems [67] by breaking the oxidation reaction down into a direct irreversible process,  $A \to C$  and indirect one,  $A \to B \to C$  through a combination of Uhlig's charge buildup concepts and integrated rate equations published by Alberty and Miller [68]. By doing so, the oxide growth curve is a product of competition between the direct and indirect processes. The resulting formula describing the dependence of oxide height on time is quite elaborate and contains four rate constants. One of the most interesting results from Dagata et al. 's model is the existence two different oxidation regimes where an initial transient mode is followed by a steady growth state. In the transient regime, both power and direct log, as well as the new Alberty-Miller equations are equivalent. However, once the oxidation time increases past 500 ms (at least for silicon) the Alberty Miller equations seem to better follow existing experimental data. However, in light of recent results published by Lazzarino *et al.* [51] contradicting certain claims about Dagata's space charge, the close agreement of Dagata's model with experimental results might simply be a result of over-parametrization.

In conclusion, as one can see, there is presently no all-encompassing, authoritative model describing SPM local oxidation. Both theoretical efforts by Dagata *et al.* [48, 49, 67] and Dubois & Bubendorff [38] have concentrated on describing the oxidation kinetics at the expense of obtaining the correct linear relation between h and V. On the other hand, Stiévenard *et al.* [36] correctly obtain  $h \propto V$  while their inverse-log h(t) form has been rejected by most. Ironically, it is the empirical relations such as Eq. 2.8 that seem to work best. This fact should probably come as no surprise considering the vast number of parameters that can affect the SPM oxidation process. In chapter 4, I will put the all the models to the test by comparing their predictions to our experimental results for GaAs.

## **Experimental Setup**

#### 3.1 The Atomic Force Microscope

The AFM operating principles are surprisingly simple. The sample is mounted on the end of a cylindrical piezoelectric tube which is fixed at the other end. A voltage is applied to the tube, called the scanner, in such a way that the sample is moved in a raster pattern beneath a sharp probe. As this probe encounters features on the surface, a flexible cantilever on which it is attached is deflected. An optical detection mechanism monitors the cantilever's vertical deflection and passes this information onto a feedback circuit. This circuit varies the z voltage applied to the piezo so that a constant cantilever deflection, and thus constant force, is maintained.



Figure 3.1: The AFM optical detection system (courtesy of Veeco Instruments, Santa Barbara, CA.).

The optical sensor is composed of a laser beam that shines onto the tip of the cantilever and is reflected into an array of four photodiodes (Fig. 3.1). As the can-

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#### 3: Experimental Setup

tilever is deflected, the reflected laser beam will move across the top and bottom photodiodes. Thus, the voltage difference between the vertical diodes is directly related to the cantilever deflection and to the topography of the surface being imaged. The particular microscope used in our experiments, shown in Fig. 3.2, has the additional capability of measuring frictional forces by also using the difference signal between the horizontal photodiodes which varies with the torsional forces exerted on the cantilever.



Figure 3.2: The Digital Instruments lateral force microscope (courtesy of Veeco Instruments, Santa Barbara, CA.).

To be able to adequately follow the contours of a surface, a certain minimal contact force must be maintained. This force can be adjusted with the use of the setpoint voltage, which is defined as the desired voltage that must be sustained by the AFM optical feedback loop while the microscope is scanning. In other words, as the sample is scanned, the z piezo voltage is continuously adjusted in order to maintain a constant cantilever deflection, and thus contact force, that produces a photodiode difference voltage equal to the setpoint. When the AFM operates in such a manner, it is said to be in contact mode (C-AFM). Ideally, the setpoint should be adjusted such that minimal force is applied to the surface, otherwise it may be damaged by the tip. However, large contact forces can also been used as a lithography technique, as we will see in chapter 5.

In certain situations the necessity of applying a force, albeit very small, can be very problematic. For example, attempts at imaging biological materials usually end up destroying the samples. Even if a sample is highly resistant to physical damage, the AFM probe may not be, and might eventually become dull. For applications requiring conductive tips, such as SPM local oxidation, tip use is particularly worrisome since the conductive coating is usually quite thin and may wear off. For these reasons, two alternative AFM operation modes have been developed: tapping and non-contact modes. In non-contact AFM microscopy (NC-AFM), a cantilever vibrating at its resonant frequency is brought close to the sample, with typical tip-sample separations on the order of 10–100 Å. Changes in this distance, because of topographical surface features, will induce changes in the cantilever's resonant frequency. This is explained by the dependence of this frequency on the force gradient experienced by the cantilever. Since the van der Walls forces felt by the cantilever are sensitive to the tip-sample separation, surface topography can therefore be tracked by changes in the cantilever's vibration frequency. Tapping mode (TM-AFM) is a combination of both C-AFM and NC-AFM modes. In this scheme the cantilever is also vibrated, but in very close proximity to the surface such that the tip lightly taps the sample in each cycle. Here, the feedback mechanism is based on the vibrational amplitude since surface features will either restrict or allow a greater cantilever movement.

#### 3: Experimental Setup

From the perspective of SPM oxidation, each method has its own advantages. C-AFM oxidation can be very fast with writing speeds of 10 cm/s having been reported [69], but probe erosion can cause poor reproducibility and pattern widening. Features written with NC-AFM and TM-AFM, on the other hand, have excellent reproducibility and better resolution since the tip does not wear [24, 70]. The tradeoff is that in these modes writing speed is generally limited to values below 20  $\mu$ m/s [40]. Regardless of the pros and cons of the various writing modes, all experiments described in this thesis have been performed in contact mode since this is the only one supported by our microscope.

#### 3.2 The Lithography Circuit

Apart from high contact force scratching, our AFM did not have any inherent lithography capabilities. Therefore, additional circuitry was needed to apply a bias voltage between the sample and the AFM tip (Fig. 3.3). The sample was grounded by directly



Figure 3.3: The AFM lithography circuit is virtually identical to that of a conventional electrolytic cell. In the case of SPM local oxidation, the thin water layer that is adsorbed to the surface acts as the electrolyte. A 100 M $\Omega$  resistor has also been included to limit the magnitude of potentially damaging current spikes.

connecting its surface with indium contacts. A 100 M $\Omega$  current-limiting resistor was placed in series as a precaution against spontaneous large current bursts which can damage the tip. The electrical connection to the AFM probe was made via the conductive cantilever retention arm. A direct connection to the cantilever would have

#### 3: Experimental Setup

been both impractical and difficult to implement, on top of having the undesirable effect of transmitting vibrations to the tip.

Cantilevers are held onto a mount with a spring spring retention mechanism and then loaded into the microscope's head. Since the original cantilever holder was made out of steel, when loaded it became electrically connected to the rest of the microscope and thus any bias voltage applied to the tip would spread through the mount and across the whole system. To overcome this problem, I constructed a plexiglass replica of the original steel cantilever holder (Fig. 3.4). In this new holder, only the cantilever retention arm is conductive, allowing a voltage to be applied to the tip without affecting the rest of the system.



Figure 3.4: Plexiglass cantilever holder diagram. The cantilever is held into place by the retention arm.

Unless otherwise noted, silicon tips with a radius of curvature of 35 nm and a 25 nm thick conductive TiO coating were used [71]. The particular choice of coating was based upon a need for mechanical, electrical and chemical stability—areas where other

conductive coatings such as Au, Pt, Cr, Ni were found to be inadequate [20]. The spring constant of the cantilevers was rated at 0.12 N/m, although the manufacturer states minimum and maximum values of 0.03 and 0.30 N/m with 0.12 N/m as being typical. For this reason it is impossible to calculate the exact contact force, although it was always minimized as much as possible in order to prolong the lifetime of the tips. As for the samples, since the ultimate goal was to pattern quantum devices onto GaAs/AlGaAs heterostructures, study was limited to the local oxidation of GaAs, using n-doped GaAs(110) samples.

#### 3.3 Automation of the Lithography Process

Apart from the conducting cantilever holder, another issue that had to be resolved was the automation of the lithography process. To control the tip's position, scripts were written in a special C programming language adapted to the microscope and then executed from the AFM software control interface. These scripts provided control of the AFM tip's position, speed, as well as voltage bias through the use of the microscope's analog voltage output. However, the maximum analog output voltage was limited to 10 V which was insufficient for proper oxidation tests. On top of this, a sudden large current draw could potentially damage the microscope's electronics. On the other hand, simply using an external power supply was not an acceptable solution since in this case it would not be possible to control the voltage from within the AFM software environment.

To overcome these problems, the scheme displayed in Fig. 3.5 was implemented: a Keithley 2400LV sourcemeter reads the AFM output voltage and relays it to a Labview program running on a workstation computer. This program multiplies the incoming voltage value by a numerical factor of my choice, which was usually set to a value of 10. Then, the new voltage is relayed to a second sourcemeter which in turn proceeds to apply this bias across the tip/sample junction. In this manner, I was no longer limited by the AFM output and could use the full  $\pm 40$  V range of the Keithley

#### 3: Experimental Setup



Figure 3.5: SPM local oxidation logistics. A lithography script sets the AFM analog output voltage, which is relayed to the workstation by the first sourcemeter. Here the voltage amplitude is multiplied by a pre-specified numerical factor and sent to the second sourcemeter, which proceeds to apply this new value across the tip-surface junction.

sourcemeters.

### 3.4 Environment Control

Usually, experiments were made in ambient atmosphere. In these situations, humidity and temperature were closely monitored for the duration of the experiment and were found to be very stable as a result of the building's climate control. To observe the effects of different gases on the lithography process, a plexiglass enclosure was constructed with separate intake and outtake valves so that the gaseous contents could be regulated (Fig. 3.6). The environment control chamber was also built with a series of bypass valves allowing the precise control of humidity by regulating the ratio of dry N<sub>2</sub> to that of water-saturated N<sub>2</sub> produced by diverting a portion of the N<sub>2</sub> through a water filled beaker (shown in Fig. 3.7).

## 3.5 Data Analysis Methodology

To study SPM oxide characteristics I proceeded to drawing a series of lines. As can be seen from Fig. 3.8, even when the oxidation parameters are identical, the resulting lines are not always of uniform height or shape. For this reason, at least a dozen lines were drawn for each set of parameter values (like voltage and writing speed).

#### 3: Experimental Setup



Figure 3.6: AFM, along with plexiglass environment control chamber



Figure 3.7: Gas control apparatus consisting of gas sources and two flowmeters. By varying the ratio of dry to humidified gas, the humidity within the AFM plexiglass chamber could be controlled.
#### 3: Experimental Setup

From these, average cross sections were calculated using the section tool from the Digital Instruments off-line image analysis software package. This tool allowed me to calculate an average profile along the line direction from which the data height and width (FWHM) could be extracted. This averaging process also provided an estimate on the accuracy of the results. Throughout this thesis, error estimates for each data point were calculated by taking the square root of the standard deviation, which is known as the standard error.

There was some concern that, for the smaller lines, the widths reported by the AFM might be inaccurate due to convolution effects between the tip and sample. However, these fears were alleviated by Tello *et al.* in Ref. [72] who showed that, by comparing oxide lines to features of known dimension, the AFM does indeed accurately reproduce oxide line topography down to heights of 1 nm and widths of 15 nm.



Figure 3.8: AFM images of oxide lines produced with a tip bias of -12V. Scan size is 5  $\mu$ m by 5  $\mu$ m, with a z range of 15 nm. Lines are on average  $3.3 \pm 0.2$  nm high.

On a last note, I should mention that in order to eliminate any confusion about the writing parameters used during a particular test, each new series of identical lines

### 3: Experimental Setup

was identified with a label describing the trial parameters. For example, when testing the dependence of h on V, the tip velocity was fixed while the voltage was varied—an appropriate label would then state the test voltage, and its polarity. An example is shown in Fig. 3.9 for test voltages of -11 V and +25 V<sup>1</sup>. Regardless of testing parameters, the label was always written with a bias that produced clearly visible oxide features, usually with a voltage of -15 V.



Figure 3.9: Test patterns were always preceded by a label indicating important lithography parameters. The series of lines shown on the left were written with V=-11 V, hence the label M11 ("M" stands for minus). For conditions producing faint, or non-existing features such as a positive tip bias (right image, where "P" stands for plus), the label would also serve as proof that the trial was successfully completed.

<sup>&</sup>lt;sup>1</sup>As we shall see in the next chapter, it is also possible to pattern features using a positive tip bias.

# 4

## Oxide Charaterization

From the discussion of current theoretical descriptions of SPM oxidation, it is apparent that a lot of work remains to be done before a definitive understanding of the process can emerge. The current models are still very simplistic and generally focus on the behaviour of one particular variable at the expense of others. In order for a complete theory to emerge, it is vital to have a strong empirical foundation on which to build it. With a few exceptions [43, 44, 45, 58, 59, 73, 74, 75], most of experimental research has focused on the study of silicon, while comparatively few reports exist on the characterization of the oxidation process in GaAs. In this chapter, I will present the results of my study of the SPM oxidation on GaAs, and how it is affected by bias voltage, writing speed and environment. When possible, my findings will be compared to the theoretical predictions of chapter 2.

## 4.1 Bias Voltage

I begin by examining the role of bias voltage. For most of the trials, at least a dozen oxide lines were drawn for each voltage value. From these, average cross-sectional line heights, widths (FWHM), as well as aspect ratios were calculated. Experimental conditions such as temperature and humidity for each trial are summarized in table 4.1. To simplify the discussion, I have ordered the tests according to relative humidity—a quick glance at table 4.1 reveals the presence of three groups. These will be referred to as the low (31–33%), medium (43–47%) and high humidity (57%) ranges throughout

the rest of this thesis. For each entry in table 4.1, a new tip was employed and was used for the duration of the trial. For our first series of experiments between June  $14^{th}$  and July  $5^{th}$ , a proper testing methodology hadn't yet been established and as a consequence only one line was drawn per voltage value. For these tests, the error represents the difficulty of precisely determining the size of features due to the finite image resolution.

Date	Relative Humidity	Temperature	Writing Speed
	(%)	(°C)	$(\mu { m m/s})$
December 4–9	33	23	0.2
December 10–12	31	23.5	0.2
September 5	33	22	0.1
June 14	45	22	0.1
June 18	47	23	0.1
July 5	45	21	0.1
August 9	43	22	0.1
August 16	57	25	0.1

Table 4.1: Experimental conditions for voltage trials with a negative bias

## 4.1.1 Oxide Height and Depth

The dependence of height on bias voltage is shown in Fig. 4.1. At first glance, my results indicates that the linear relation (Eq. 2.7) derived by Stiévenard *et al.* is correct. However, if the data is presented in a different light, such as in Fig. 4.2, power or exponential laws seem almost just as convincing. To ascertain the proper form, linear regressions were made for each of the scenarios and are summarized in table 4.2. From inspection we see that within each of the separate humidity ranges, the fitting parameters are clearly in closest agreement for the linear model. For this



Figure 4.1: Dependence of oxide line height with bias voltage for (from top to bottom) low, medium and high humidity.

Humidity	Linear	Log-Log	Semi-Log
	h = mV + b	$h = 10^b V^m$	$h = 10^{mV+b}$
31% (Dec. 10–12)	$m=0.29\pm0.03$	$m = 1.29 \pm 0.07$	$m = 0.014 \pm 0.002$
	$b=-0.98\pm0.04$	$b=-1.02\pm0.05$	$b=-0.10\pm0.02$
33% (Dec. 4–9)	$m = 0.248 \pm 0.04$	$m=0.71\pm0.01$	$m = 0.0348 \pm 0.0006$
	$b = -0.48 \pm 0.03$	$b=-0.29\pm0.01$	$b = -0.021 \pm 0.008$
33% (Sept. 5)	$m = 0.295 \pm 0.003$	$m = 1.381 \pm 0.014$	$m = 0.0417 \pm 0.0005$
	$b = -0.6 \pm 0.4$	$b = -1.08 \pm 0.1$	$b = -0.091 \pm 0.007$
43% (Aug. 9)	$m = 0.74 \pm 0.01$	$m = 2.6 \pm 0.05$	$m = 0.109 \pm 0.002$
	$b=-4.1\pm0.1$	$b=-2.12\pm0.05$	$b = -0.67 \pm 0.03$
45% (June 14)	$m = 0.8 \pm 0.2$	$m=2.2\pm0.1$	$m = 0.069 \pm 0.007$
	$b = -5 \pm 2$	$b = -1.8 \pm 0.2$	$b = -0.3 \pm 0.1$
45% (July 5)	$m = 0.62 \pm 0.04$	$m = 1.7 \pm 0.2$	$m = 0.049 \pm 0.006$
	$b = -3.28 \pm 0.6$	$b = -1.2 \pm 0.2$	$b = -0.02 \pm 0.1$
47% (June 18)	$m = 0.61 \pm 0.05$	$m = 1.91 \pm 0.21$	$m = 0.054 \pm 0.005$
	$b = -3.2 \pm 0.5$	$b = -1.55 \pm 0.22$	$b = -0.13 \pm 0.09$
57% (Aug. 16)	$m = 0.580 \pm 0.008$	$m = 1.66 \pm 0.023$	$m = 0.059 \pm 0.007$
	$b = -2.41 \pm 0.06$	$b = -1.13 \pm 0.02$	$b = -0.08 \pm 0.08$

Table 4.2: Fitting results for data presented in Fig. 4.1.

reason, I conclude that the linear dependence of height on bias voltage proposed by Cabrera & Mott, and Stiévenard *et al.* is correct.

The depletion of the 2DEG in GaAl/AlGaAs heterostructures is directly related to the depth of the oxide patterned on the GaAs cap layer. Because of this, it is also important to understand the relation between oxide height and depth. To do so, the oxide lines of the December  $4^{th}$ -12<sup>th</sup> voltage trials were selectively etched away in a 10% aqueous HCl solution for 1 minute. The GaAs itself is resistant to the effects



Figure 4.2: Linear, log-log and semi-log plots of high humidity data (August  $16^{th}$ ).

of HCl [76], so only the patterned oxide features, along with a few atomic layers of native oxide are removed. An example of a series of oxide lines written before and after the etching process is presented in Fig. 4.3. For this particular series of lines, the ratio between height and depth is  $0.88 \pm 0.06$ . However, an exact ratio for the entire series of December trials was impossible to calculate because, unless there was some distinguishing feature such as the two dots at the top of the rightmost line in Fig. 4.3, it was difficult to be certain that the same area was being compared. Nevertheless, the results show that, on average, oxide penetration depth is roughly equal to its protruding height. A height/depth ratio close to unity has also been observed for silicon by Morimoto *et al.* [50].

The choice of the lines shown in Fig. 4.3 was quite deliberate. A number of times I have observed what seems to be splitting of the topmost part of the oxide lines, and in extreme cases, two distinct and separate lines have even emerged. This split-wire effect has also been observed by others [48, 26] and seems to be partly due to the Coulomb attraction that appears between the tip and sample when a bias voltage is applied. For small tip biases, this Coulomb attraction is too weak to put a dent into the oxide. However, as the tip bias increases, so does the electrostatic attraction and eventually the tip starts to dig into the oxide line. This effect is compounded by the AFM feedback mechanism which interprets this increase in cantilever bending as the presence of a dip on the sample surface. Consequently, the AFM increases the contact



Figure 4.3: AFM 1.0  $\mu$ m by 1.0  $\mu$ m scan of lines written with a bias of -10 V, before (left) and after (right) etching in 10% HCl.



Figure 4.4: Oxide line height and trench depth after 1 min etch in a 10 % aqueous solution of HCl. These particular lines were drawn with a bias voltage of -10 V and speed 0.2  $\mu$ m/s.

force in an attempt to properly track this imaginary hole. There was some concern that this splitting would be mirrored by the oxide growth within the sample, thus limiting its penetration, but a cross-section of the etched features of Fig. 4.3 indicated

that this is not the case. Interestingly enough, if the dip at the top of the oxide lines in Fig. 4.4 is reversed, both the oxide height and trench depth have an almost perfect match, as seen in table 4.3. In Ref. [43], the height/depth ratio for GaAs is reported to be about 1/2. However, the lines shown in Ref. [43] seem to suffer greatly from the split wire effect, which could account for the small ratio that was obtained.

Line	$\operatorname{Depth}$	$\operatorname{Height}$	Height + Dip
	$(\pm 0.1 \text{ nm})$	$(\pm 0.1 \text{ nm})$	$(\pm 0.2 \text{ nm})$
a	3.5	3.0	3.6
b	3.0	2.6	3.0
c	4.5	3.7	4.7
d	4.1	3.5	4.0
е	2.9	2.9	2.9

Table 4.3: Comparison of oxide line height and trench depth for the data in Fig. 4.4. The trench depth is roughly equal to the sum of line height and notch depth.

### 4.1.2 Threshold Voltage

Throughout the literature, the presence of a threshold voltage  $(V_{th})$ , such as seen in Fig. 4.1, has been observed for a number of different types of substrates. In all cases, this threshold can be explained by a combination of voltage loss, AFM operational mode and sample doping. First, any additional resistance in series along the lithography circuit will cause a drop in the voltage originally intended for the tipsurface junction. For example, an increase of  $V_{th}$  has been observed for experiments made with soft conductive coatings such as gold and platinum that are prone to wear, resulting in an increase in  $V_{th}$  as the probe is stripped [45, 46]. Similarly, oxide growth on the tip or sample will have the same effect [77]. For this reason, silicon tips without additional protective coatings are to be avoided since they are especially vulnerable to oxidation [39, 40]. An important role is also played by the AFM operational mode.

In Ref. [42], Chien *et al.* observed a two-fold increase in  $V_{th}$  when switching from contact mode to tapping mode lithography which they attribute to a reduction of the effective electrical field in tapping mode. The presence of a threshold voltage in tapping mode has also been confirmed by Servat *et al.* in Ref. [25]. As for non-contact AFM lithography,  $V_{th}$  is mainly associated with the electrical field required to polarize the adsorbed water film and form an electrolytic bridge between the tip and sample [70, 78, 79]. Finally, there have been reports that sample doping also has an effect on  $V_{th}$ . For *p*-type samples,  $V_{th}$  as well as the slope dh/dV have been observed to vary with dopant concentration [22, 39, 40], while *n*-type materials did not exhibit such behaviour and showed a very small threshold.

Date	Relative Humidity	Threshold Voltage
	(%)	(V)
December 4–9	33	$3.4 \pm 0.4$
December 10–12	31	$2.0 \pm 0.3$
September 5	33	$2 \pm 1$
June 14	45	$6\pm 3$
June 18	47	$5.2\pm0.9$
July 5	45	$5\pm1$
August 9	43	$5.5 \pm 0.2$
August 16	57	$4\pm 1$

Table 4.4: Threshold voltages obtained from table 4.2

In my case, the linear fit results in table 4.2 ( $V_{th} = -b/m$ ) indicate the presence of a different threshold voltage for each humidity grouping. Since my samples originated from the same n-GaAs (110) wafer, I can exclude doping effects. The seemingly larger threshold for medium and high humidity may suggest that in these cases, the sample or the tip has been oxidized. However, the same sample was used for both

August 9<sup>th</sup> and September 5<sup>th</sup> trials so the drop in  $V_{th}$  cannot be attributed to a humidity-triggered growth of the native oxide since any additional thickness would have remained during the lower humidity trial in September. For similar reasons, tip oxidation is disregarded because  $V_{th}$  would have become progressively larger with time since the tips were all purchased at the same moment and stored next to each other in ambient atmosphere. Furthermore, because a new tip was used for each trial and considering the hardness of TiO, stripping of the conductive layer was most likely insignificant.



Figure 4.5: SEM image of an AFM tip before (left) and after (right) writing a series of 15 lines at a bias of -15 V.

While the tips may not necessarily lose their coating or become oxidized, an increase in  $V_h$  could still be observed if they became contaminated during the lithography process. To look into this possibility, a scanning electron microscope image was made of a new tip before and after writing a series of oxide lines. As can be seen from Fig. 4.5, some contamination has formed at the tip apex which could possibly affect the electrical properties of the tip, explaining the presence of a threshold voltage. Supposing the level of contamination depends on humidity, these observations could also explain the relationship between threshold voltage and humidity observed in table 4.4.

I conclude the discussion of  $V_{th}$  by noting that even though my results show a

definite existance of a threshold voltage, these results, as well as those published in the literature, cannot determine whether this threshold voltage results from a true physical limitation of the oxidation process or rather expresses the fact that the bias was applied for too little time. Instead, our results must be simply interpreted as a description of the oxidation process for a particular writing speed, or exposure time. It is entirely possible that successful surface modification could be achieved even for a vanishing bias voltage, provided the pulse is applied for a sufficient amount of time. By applying voltage pulses lasting in excess of 1000 seconds, Avouris *et al.* had observed no clear bias threshold, even for voltages as low as 2 V [15]. Cursory evidence has also been presented by Barniol *et al.* in 1995 [80] that the contact potential between an STM tip and the silicon surface was enough to initiate an oxidation reaction. This corresponds well with the model of Cabrera and Mott where the electrical field arising from the contact potential between adsorbed oxygen molecules and a metal surface is sufficient to initiate the oxidation reaction, even at low temperatures.

### 4.1.3 Lateral Resolution and Aspect Ratio

Just as it was observed for height, the line width also has a linear dependence on voltage (Fig. 4.6). The aspect ratio (defined as height/width) seems to increase with voltage until a plateau is reached around 10 V. The exception to this rule are the medium humidity trials where the aspect ratio shows no clear sign of stabilizing. However, we have to remember that the statistics for all but one medium humidity test (June 14<sup>th</sup> to July 5<sup>th</sup>) are not as reliable as the rest of the tests since only one line for each voltage value was drawn in these cases.

Ideally, lines should have the highest possible aspect ratio such that tall features can be patterned without sacrificing resolution. Thus, according to the data, voltages above 10 V are preferable. However, I will show in the next section that large oxide discharges occurring at higher voltages set a practical upper limit to the bias voltage that can be used for SPM local oxidation lithography.



Figure 4.6: Dependence of line width and aspect ratio with (negative) bias voltage for low, medium and high humidity (from top to bottom).

### 4.1.4 High Bias Voltage Growth

While the linear dependence of oxide height with bias voltage suggests unlimited oxide growth, this is unfortunately not the case. At high voltages (> 25 V), large oxide discharges begin to appear which create unpredictable oxide piles on the sample surface (Fig. 4.7). Avouris *et al.* proposed that hot electrons ejected by the AFM tip through a field emission process are responsible for this effect [15]. When these electrons collide into the conduction band of the growing oxide, avalanches of secondary electrons of lesser energy may occur. These stochastic avalanches open up a new "fast" oxidation pathway by increasing the number of reactive agents through ionization. As a result, large and unpredictable oxide discharges can occur that are potentially damaging to the tip. Following such a discharge there usually was a noticeable degradation in image and line quality. Control of the junction current has



Figure 4.7: Large oxide discharge typically encountered at high bias voltage. In this particular case,  $V=-30~\mathrm{V}$ 

proven useful in preventing tip damage [81], and in limiting the extent of these discharges. It is for this reason that a 100 M $\Omega$  resistor was included in the lithography circuit. Since I have at times observed discharges with heights in excess of 50 nm, it would be very interesting if some method was found to control these oxide outbursts. Preliminary trials with different values of current-limiting resistors (see Fig. 4.8) have shown some promise but more work needs to be done before any conclusions can be drawn.



Figure 4.8: Use of smaller current-limiting resistance to control oxide discharges. This particular trial was made with a bias of -15 V and a resistance of 1.0 M $\Omega$ , instead of the usual 100 M $\Omega$ . On average, lines are 10 nm high, while the tallest "blobs" exceed 25 nm in height.

### 4.1.5 Positive Voltage Bias

In the conventional Cabrera and Mott formalism, it is argued that the transport of ions from the metal/oxide to the oxide/air interface is aided by the electrical field, as shown in chapter 2. In the case of SPM oxidation however, it is widely believed that oxygen species such as OH<sup>-</sup>, instead of ions, diffuse to the oxide-semiconductor interface. Should the SPM tip be positively biased, the resulting electrical field would then hinder instead of promote the diffusion of negatively charged species towards the semiconductor surface, preventing the oxidation reaction from proceeding.

To explain surface modification with a positive bias, it has been suggested that when the voltage polarity is reversed, it is  $H_3O^+$  ions who instead diffuse towards the surface [82]. Supposing that this is the case, the oxidation mechanism should then be the same regardless of tip polarity. In Ref. [80], Barniol *et al.* suggested that it was indeed possible to use both positive and negative voltages for STM oxidation on Si. However, only a small range of bias voltages between -1.5 and +1.5 V was investigated, making it difficult to reach any definite conclusions using these results. On the other hand, some authors report a complete lack of any surface modification when positive tip biases are used in AFM experiments [83]. These conflicting results could be reconciled by supposing that for AFM local oxidation, a larger threshold exists in the case of positive tip biases. This could explain the lack of oxidation with positive voltages in Ref. [83] since their instrumental setup was limited to a range of biases between -10 and +10 V. Similar results have also been reported by Sugimura and coworkers [61] where the modification with a positive tip bias was barely perceptible. Once again though, higher voltage ranges were not investigated (experiments were made between +5 and -5 V).

To shed light onto this mystery, I have investigated lithography with a positive tip bias. The first series of positive voltage trials were made on the same day, and with the same tip, as the negative voltage trials of September  $5^{th}$  such that experimental variations were minimized. This allowed for a fair comparison between both polarities to take place. A second trial was made on December  $16^{th}$ , and experimental conditions for each test are summarized in table 4.5 below.

Trial	Rel. Hum.	T°	v
	(%)	(°C)	$(\mu m/s)$
Sept. 5 (Neg.)	33	22	0.1
Sept. 5 (Pos.)	33	22	0.1
Dec 16 (Pos.)	31	23	0.2

Table 4.5: Experimental conditions for positive voltage trials

I will begin by discussing the results of the September  $5^{th}$  trial, where positive



Figure 4.9: Height dependence on positive bias voltage for the September  $5^{th}$  trial.

tip voltages were investigated in the range of 10.0–38.0 V. Results for this trial are shown in Fig. 4.9. A peculiar aspect about this figure is the surprisingly large fluctuations in oxide height from one data point to the next. In particular, height values corresponding to voltages of 28.5, 30, 31.5 and 33 V are unusually low.

To explain these results, I will suppose that with a positive voltage bias, there is an extra mechanism at work, or requirement that has to be met, in order for the oxidation to proceed. The larger threshold voltage is, by itself, an indication that some aspect of the lithography process is different for positive voltages, so this supposition is not that far-fetched. Furthermore, I will suppose that if one of these extra requirements is not met, patterning may still proceed, but at a much slower rate. The small feature heights observed in Fig. 4.9 would then correspond to the scenario where one of the supplemental ingredients was missing, while the larger features represent normal



Figure 4.10: Height dependence on bias voltage for both positive and negative voltages, after removal of the four low-lying data points in Fig. 4.9.

SPM oxide growth where all the requirements are met. Following this argument to its logical conclusion, should the 4 deviant points be removed, the rest of the lines should follow the same oxidation mechanism as the negative bias case, and have the same voltage dependence. Indeed, this is what is observed in Fig. 4.10: slopes for the positive and negative branch are  $0.28 \pm 0.03$  nm/V and  $0.295 \pm 0.003$  nm/V respectively. The only difference between both polarities is the presence of a larger bias for the positive branch, which would explain why it was missed by the authors of Ref. [83].

This dual-mode positive oxidation theory might seem a little far-fetched, yet similar behaviour has been shown to exist in the case of non-contact SPM lithography and the formation of a water meniscus. In non-contact mode, García *et al.* have seen that the existence of a water bridge plays a crucial role in the SPM oxidation process



Figure 4.11: Height dependence on positive tip bias for December  $16^{th}$  trial

[78] and that without this bridge the oxidation did not proceed. In another example, Snow *et al.* have observed an increase in the oxide growth rate by a factor of  $10^4$  when writing to hydrophilic surfaces instead of hydrophobic ones [41].

To gain more insight into the positive voltage "oxidation", a second study was made in December. In this case, oxide height never made it past 0.5 nm, as seen in Fig. 4.11. This result indicates a strong resemblance between this experiment and the 4 points that were removed in Fig. 4.10. As a definitive comparison between the negatively and positively patterned features, the lines were etched away by dipping in an aqueous solution of 10% HCL for 1 minute. Surprisingly, instead of leaving a shallow trench, the positive bias lines left behind a series of little dots, as seen in Fig. 4.12. Averaging along the dot direction (Fig. 4.13) reveals a periodicity of 128 nm which corresponds exactly with the periodicity of the original positive bias features. This, coupled with the observation that the droplets are confined to the area which

used to hold the lines, confirms that these spots are indeed due to the positive lines. Examination of negative lines having started out with the same height do not show the presence of such dots, showing instead the presence of trenches, as is expected since GaAs oxide is easily dissolved by the HCL dip. These observations lead to the conclusion that a positive bias must affect the sample surface differently than a negative bias, contrary to what is currently believed. Unfortunately, in September certain technical issues related to pattern etching had not yet been resolved so the positive voltage features shown in Fig. 4.10 were not etched away. Further tests would be needed to verify if features produces with a positive bias always leave a series of depositions instead of the usual trench.

In light of the etching results, an alternative explanation akin to metal deposition could be put forth in order to explain the properties of features produces with a positive voltage bias. When a tip with a conductive coating, such as gold, is placed in close proximity to the surface, a bias voltage can be used to cause an increase in the tunnelling current across the tip-surface junction due to the presence of fieldemission electrons. This increase in tunnelling current can in turn produce heating at the tip apex, and consequently melt the conductive coating off the tip, resulting in a metal deposition on the sample surface [84]. Indeed, Barniol et al. reported that for large positive tip voltages, metal-deposition was noticed with a Pt/Ir tip [80]. While this phenomenon might explain the dots that were left behind after etching, metal deposition seems unlikely since the TiO coated tips used in my experiments are extremely stable. In the unlikely event that the TiO coating does detach under a positive bias, signs of damage to the tip should logically be noticeable. For this reason, a scanning electron microscope (SEM) was used to test a few tips before and after producing a series of oxide lines, using both positive and negative bias voltages. As expected, SEM images confirm that no material was lost from either positively or negatively biased tips, even with voltages of  $\pm 30$  V (Fig. 4.14). What was seen however, was the presence of some sort of accumulation at the tip's apex which was



Figure 4.12: AFM image of dots left after the etch of +38 V features. Scan size is 5  $\mu$ ms.



Figure 4.13: Periodicity check for dots left after etch of +38V features revealing that the dots are separated by the same distance as the original lines.

greater for the positively biased test. This may be coincidence, or could possibly explain the larger threshold voltage observed for the positive bias. Perhaps when it is biased positively, the tip is oxidized through some anodization mechanism which would increasing the necessary voltage for the usual lithography reaction to proceed. This could also explain the abnormally large height fluctuations in Fig. 4.9 since this tip-oxide may not be very stable and may break off during or between the different lithography trials and imaging sequences.



Figure 4.14: SEM images of TiO AFM tips before (left) and after (right) use. Top images are for tip the bias of +30V, while bottom images are for -15V.

## 4.2 Writing Speed

The vast majority of systematic studies of the oxidation process have focussed on the kinetics of the reaction. As seen in chapter 2, the relation between oxide height and time (or writing speed) can be cast into many contradicting forms. We have seen that there are currently three different types of relations describing the time dependence of the oxidation reaction: the inverse logarithmic, direct logarithmic and power law relations.

There are two different methods to test the time evolution of the oxidation reaction. The first consists of drawing oxide dots while varying the pulse duration. The second is to draw a series of lines with different tip writing velocities. Even though both methods should give equivalent results since the writing speed is inversely proportional to the exposure time, there have been reports that, while the kinetics are the same, the maximum achievable oxidation rate for the line writing method can be greater by a factor of up to  $10^4$  [41]. This is explained by a certain minimal exposure time necessary to create a water bridge in the pulsed voltage experiments. According to the authors of Ref. [41], this minimal exposure time can be eliminated by the use of hydrophilic substrates that maintain the water bridge between the tip and surface for all anodization voltages. Due to the greater relevance of lines in the fabrication of quantum structures by SPM lithography, time dependence was tested using a series of lines, and not dots.

### 4.2.1 Line Height

I begin by examining the oxide height dependence on writing speed. Results presented in Fig. 4.15 seem to indicate that a power law provides the best description of the data. When using an inverse logarithmic form, a clear deviation from the straight line for low writing speeds, or alternatively, high exposure times is observed. Distinguishing between the direct logarithmic and power law relations, on the other hand, is a little more tricky. From a purely visual observation, the power law seems to be



Figure 4.15: Writing speed dependence of oxide height, presented according to the three different theoretical descriptions of the oxidation process. The experimental data was recorded with a constant voltage of -10 V, a temperature of 25°C and a humidity of 58%.

more robust and follows the data very well for the entire range of writing speeds that were tried. As for the direct logarithmic form, it diverges for the lower speeds by an amount that depends on the particular linear regression technique. Based purely on a statistical least squares fit, one could still argue that the direct logarithmic form was an appropriate description, but once the weighting of each individual point is taken into account, the diversion between the logarithmic behaviour and my results becomes very apparent. With the power law regression, the same curves are obtained with an without weighting the data points, strongly indicating that this is the correct description this data. Furthermore, the resulting power law exponent is in perfect agreement with Teuschler's result of 1/4 [22]. In this case I found  $0.26 \pm 0.02$ , even though my substrates are very different: I used n-GaAs(110) while Teushler's experiments were made on silicon(111).

As mentioned in chapter 2, Dagata et al. proposed a theory in which there were two different oxidation regimes [67]: an initial, fast growing transient stage where both lateral and vertical growth exist within the oxide, followed by a slower steady state where the growth is mostly lateral. In Uhlig's original article [65], on which Dagata's work is partly based, the presence of two separate growth regimes is also observed but the order of these states are reversed. In Uhlig's case, the fast growing comes after the initial slow growing phase. Provided that my experiment covers the right time interval, and that the direct logarithmic form is the correct one, a transition between both regimes should be seen. In Fig. 4.16, I show a plot of h versus 1/v instead of the usual v, which is equivalent to plotting h versus t, except for a missing constant of proportionality. As seen on Fig. 4.16, the results seem to support the presence of multiple growth regimes, however the order of these contradict the predictions of Dagata et al. since in my case it seems that in the transient regime the growth is slow, after which it speeds up for longer pulse durations. Instead, my growth rate seems to follow the same behaviour proposed by Uhlig in Ref. [65]. In Uhlig's model, when the thickness of the oxide increases, the space charge density goes from



Figure 4.16: Transition from a low growth rate to a high growth rate.

having a uniform distribution to being sparsely arranged. Eventually, space charge accumulation ceases for large oxide thicknesses. The oxide then becomes electrically neutral and, consequently, in this limit oxide growth is no longer affected by the presence of space charge. It should remembered, however, that Uhlig's model was developed to explain the low-temperature oxidation of metals and not SPM oxidation.

In light of these observations, it seems that it is a power law that most probably describes SPM oxidation kinetics. While the direct log form cannot be readily dismissed due to the possible existence of 2 separate growth regimes, clashes between theoretical predictions and experimental data turn the direct log form into an unlikely candidate. As for the inverse log form, Fig. 4.15 shows that it is clearly inadequate, especially at low writing speeds.

### 4.2.2 Line Width and Aspect Ratio

Based upon the conclusions of the previous section, only log-log plots of the line width and aspect ratio will be presented here in order to lighten the presentation. As mentioned in the introduction, to pattern 2DEGs embedded in GaAs/AlGaAs heterostructures, it is very important to be able to produce oxide features that reach

deep into the substrate. This would not be too problematic if lateral resolution was of no importance since we have seen that the application of very large voltage biases lead the deposition of large oxide piles that can exceed 50 nm in height (and thus depth). However, to be useful as a lithography technique, a high lateral resolution is of utmost importance and should be maintained at all costs. As seen in section 4.1.3, once the bias voltage is increased beyond 10 V there is no generally improvement in the aspect ratio. For this reason, bias voltages in the range of 10–20 volts represent the best compromise in feature height and lateral resolution.



Figure 4.17: Dependence of line width and aspect ratio on writing speed for V = -10.0 V, T = 25°C and a humidity of 58% (this data was extracted from the same oxide lines used for Fig. 4.15).

Once the optimal voltage range was established, the next step was to examine the effect of writing speed on the aspect ratio. Results shown in Fig. 4.17 indicate that the aspect ratio increases with exposure time. A maximum ratio of ~0.08 was reached for  $v = 0.01 \ \mu m/s$ , but it is difficult to say with any certainty if this is an absolute maximum since it was still on the rise. While it might have been worthwhile to investigate even slower speeds, the large x-y piezo drift effectively put an end to the trials. In 2001, Matsuzaki *et al.* have observed a similar evolution of the aspect ratio with speed for experiments made on n-doped GaAs [73]. In their case, a clear maximum was seen for  $v = 0.05 \ \mu m/s$ . As we shall see in the next few sections, a

proper control of the environment can have a much more dramatic effect on aspect ratio than writing speed. Nonetheless, my results show that a proper choice of writing speed can effectively double the aspect ratio, which is of definite significance.

## 4.3 Environment

Throughout the results so far, there has been strong indications that environmental parameters such as relative humidity can have a large effect on the oxidation process. In this section, I will examine the role of water in SPM oxidation. Then, as a consequence of the findings about relative humidity, SPM local oxidation in a pure  $O_2$  environment will be discussed.

### 4.3.1 Humidity

In a typical anodization reaction, ions are carried across an electrolyte under the influence of an applied voltage bias. The presence of an electrolyte is vital since an electrically conductive path is needed for electrons and ions to flow across and continue the oxidation process. In SPM oxidation, the electrolyte is a thin layer of water which is usually adsorbed onto the sample surface. However, even when SPM oxidation is attempted on hydrophobic surfaces, the reaction still proceeds because of the humidity content of the surroundings forms a water meniscus around the tip-sample interface when a voltage pulse is applied. For silicon, hydrophobic surfaces can be prepared by standard RCA cleaning techniques resulting in a hydrogen passivated surface [8, 85], while a similar passivation method exists as well for GaAs, involving an aqueous  $P_2S_5/NH_4S$  solution [86, 87].

The importance of a water meniscus in the SPM oxidation process cannot be overstated. For SPM experiments made in non contact mode, it was found that no oxidation would happen beneath the threshold voltage required to polarize the adsorbed water layer beneath the tip and subsequently form an electrolytic bridge across the gap [70, 78, 60, 79]. The formation of this bridge has also been observed very recently by measuring the tunnelling current across the tip-surface junction [88]: in the absence of a meniscus, the current has an exponential dependence on the tip distance from the sample, while the formation of a water meniscus transforms this dependence to a linear, ohmic one.



Figure 4.18: Effect of humidity on height, width and aspect ratio voltage rates (dh/dV, dW/dV) and dR/dV, calculated from table 4.2

Because the presence of the water meniscus is vital to the SPM oxidation reaction, it is ironic that this meniscus is also responsible for pattern widening, and thus is one of the main resolution limiting factors. To the best of my knowledge, the only systematic study of relative humidity and it's effect on SPM oxidation was made by Sugimura *et al.* in 1993 on a titanium substrate [33, 12]. Their results show that both the lateral and vertical growth rates depend on the relative humidity. It was noticed that the height of features remained relatively unaffected until extremely low humidities were used during the patterning. On the other hand, lateral growth is very sensitive to any variation in humidity. In Sugimura *et al.* 's experiments, dropping the relative humidity from 90% to 65% resulted in a lateral growth rate drop of more than 300%, while the vertical growth continued, unhampered.

Looking over the data from sections 4.1.1 and 4.1.3, we see a very similar behaviour for the slopes of dh/dV and dW/dV, that I shall call height and width voltage rates. The rates presented in Fig. 4.18 are averages of those shown in table 4.2. As we see, both dh/dV and dW/dV are influenced by humidity, with the notable exception that the rate enhancement saturates for dh/dV while it does not for dW/dV. As for the aspect ratio, because the width continuously increases with humidity, whereas the height does not, it is no surprise that the highest aspect ratio occurs for lower humidity situations. Ideally then, SPM lithography should be performed under low humidity environments.

### $4.3.2 \quad O_2$

In 1997, Avouris *et al.* speculated that the pattern widening under high humidity conditions was due to a deformation of the electrical field by the water meniscus [37]. Because of this, it is apparent that an improvement in lateral resolution would be achieved should any means be found to reduce the lateral extent of this water meniscus. As suggested by Sugimura *et al.* 's work on titanium, one of the ways of achieving a reduction of the water meniscus surrounding the SPM probe is to use a pure oxygen environment during the lithography process. Here we report that SPM lithography in a pure oxygen environment succeeds in increasing the line aspect ratio, height as well as decreasing the width.



Figure 4.19: AFM image of a series of lines written in air (left) and oxygen (right) with V = -15 V and  $v = 0.1 \ \mu m/s$ . Image area is 5 by 5  $\mu m$ .

To perform these tests, the microscope was sealed in the environment control chamber, which was described in chapter 3 and shown in Fig. 3.6. The chamber was then flushed with a high flow of  $N_2$  for 10 minutes followed by another 10 minutes of  $O_2$ . Fig. 4.19 shows two series of lines that were produced in 45% relative humidity ambiant and pure oxygen atmospheres. The relative humidity of the oxygen atmosphere was below instrumental resolution of 7%. The average characteristics of these lines are summarized in table 4.6 below.

Atmosphere	Height (nm)	Width (nm)	Aspect Ratio
Air, 45% rel. humidity	$5.1\pm0.2$	$172\pm7$	$0.030\pm0.001$
Oxygen, $< 7\%$ rel. humidity	$6.9\pm0.4$	$54 \pm 4$	$0.130\pm0.007$

Table 4.6: Average characteristics of lines shown in Fig. 4.19.

As these results show, the oxygen atmosphere is ideal for SPM oxidation: line height increases while the width decreases. As for the aspect ratio, it increases by over a factor of 4. This effect can be due to two things. First the lateral extent of the water meniscus is greatly decreased because of the low humidity. Second, the high concentration of atmospheric oxygen could increases the presence of  $OH^-$  ions within the small remaining water meniscus. In this way, lateral growth is diminished while vertical growth is unaffected by the small humidity content, which corresponds with Sugimura *et al.* 's observations on titanium [61]. I expect that a further improvement in line quality could be observed by including a pre-baking step to completely rid the surface of any remaining adsorbed water layer, and by introducing a highly reactive gas such as Ozone within the chamber during the oxidation process.

Even though the aspect ratio of the lines drawn in  $O_2$  has increased, the voltage dependence remains linear, as shown in Fig. 4.20. The properties of the height, width and aspect ratio are very similar to SPM oxides created in air. The only notable difference in the oxidation process under an  $O_2$  environment is an increase in the threshold voltage.



Figure 4.20: Oxide line characteristics in a oxygen atmosphere

# 4.4 Summary

Due to the wealth of information presented in this chapter, a review of the main results is in order. Through systematic study of the bias and time dependence of oxide height, it was concluded that the height has a linear dependence on voltage, while the oxidation kinetics are governed by a power law. It was seen that a voltage between -10 and -20 V, a writing speed below  $0.01 \,\mu\text{m/s}$  and an oxygen environment produced the highest quality oxide features along with the best aspect ratios. Positive voltage biases were also investigated and it was seen that, surprisingly, they were still able to pattern the GaAs surface. However, because of the different etching properties of features created with a positive voltage, it was concluded that a different mechanism was at work in this case.

# High Contact Force Lithography

In the previous chapter, the properties of SPM oxidation were examined in the hope that this lithography technique could be better understood and eventually used in combination with GaAs/AlGaAs heterostructures to create working quantum devices such as quantum point contacts, and quantum dots. As mentioned in the introduction, SPM local oxidation can deplete shallow 2DEGs in a process akin to a very selective etch of the heterostructure cap layer—indeed, the depletion effects remain even if the oxide is removed [31], indicating that it is the "hole" produced in the cap layer by the oxidation which is of importance. For this reason, other methods of modifying the cap layer were investigated, with the most obvious one being the direct mechanical scratching of the sample. In this chapter, I will present the results stemming from this research.

## 5.1 Experimental Setup

Two changes were made to the experimental setup discussed in chapter 3. Cantilevers with an average spring constant of 2.0 N/m ( $\sim$  10X larger than the ones used previously) were chosen, although the type SPM probes themselves remained unchanged (TiO coated silicon tips). Two different substrates were used, labelled 1-31-01.1 and 3-12-01.1, which were both GaAs/AlGaAs heterostructures that differed slightly in the thickness of the different layers (Fig. 5.1). The reason for testing two different types of substrates was to verify if the scratching had any dependence on the thickness

### 5: High Contact Force Lithography

of the different layers.



Figure 5.1: Composition of samples used in this experiment. Depth unit is the Å.

The scratching procedure was fairly simple. While the AFM was imaging, the setpoint would be changed such that the maximum possible force was applied, which resulted in the removal of material as the tip was scanned across the surface. The end result was a square pit, whose depth depended on the amount of imaging passes that were made. Control of the force applied to the sample was made through the setpoint parameter, defined as the desired voltage that must be maintained by the AFM difference feedback circuit. In normal imaging modes, the setpoint is usually set in the middle of the z-voltage range of the piezo (-10 to +10 V) to allow the greatest piezo flexibility. When one's intention is to apply the maximum possible force, the neutral cantilever deflection signal is adjusted to the end of the lower range, at -10 V, while the setpoint is set to +10 V. As a result, the AFM will drive the tip into the sample until the cantilever deflection signal increases all the way to +10 V, producing a large contact force between tip and sample. The exact correspondence between setpoint and applied force depends on the particular cantilever that is used, and will be discussed in greater detail later in the chapter. In all scratching cases below, unless

otherwise noted, the imaging resolution was set to the maximum value of 512X512 to maximize the amount of scratching passes in a given area. Also, a large scanning frequency of 10 Hz was used to increase the amount of scratching passes per unit time. Once the scratching was complete, the contact force would then be returned to normal so that the features could be properly imaged without causing any further damage. A new tip was used for each scratching test.

## 5.2 First experiments

The first experiment were made using the 1-31-01.1 sample. In this trial, three oxide strips were made after which a large contact force (produced by a difference of 10 V in the setpoint) was applied. After about 5 or 10 minutes, contact force was returned to normal and the resulting features were imaged. Results are shown in Fig. 5.1.

One of the most surprising aspects of this test was the resistance of the SPM oxide bands to the scratching procedure, which was a definite indication that the oxide had different physical/chemical properties than the GaAs substrate. After imaging the pit, oxide lines were drawn using a bias voltage of -15 V, and a writing speed of  $v = 0.1 \mu$ m/s. Average line heights and aspect ratios for the different areas outlined in Fig. 5.1 are presented in table 5.2 below.

averaging area	height (nm)	FWHM (nm)	h/w
A	$5.2 \pm 0.2$	$180 \pm 15$	$0.028 \pm 0.003$
В	$5.5\pm0.4$	$180 \pm 12$	$0.030 \pm 0.003$
С	$2.8\pm0.4$	$84 \pm 10$	$0.033\pm0.006$

Table 5.1: Line height results for different averaging areas in Fig. 5.1

When comparing results for areas A and B, it is apparent that oxide characteristics do not fluctuate depending on whether the lines were drawn inside or outside of the pit, indicating that there is no difference between scratched and unscratched surfaces.


Figure 5.2: 8  $\mu$ m by 8  $\mu$ m AFM image of scratch features on 1-31-01.1 sample. The z-range is 20nm, pit depth is on average about 5.7 nm. At its deepest, the pit was 8.9nm. Large, bright bands are the result of SPM anodic oxidation before the digging occurred indicating that the oxide is a lot more resistant to mechanical strain than the GaAs substrate. Boxes represent averaging areas for results in table 5.2.

Supposing that the native oxide present on GaAs takes a few hours to form and considering that the lines where drawn immediately following the scratching, the small variation between oxide features residing in boxes A and B indicate that the native oxide layer present on the GaAs surface is rather thin, probably on the order of a monolayer of two, as is expected for GaAs.

Another interesting aspect of this data is seen by comparing results for region C to those of A and B. It seems, from table 5.2, that the average height of oxide features in region C is smaller, indicating that the oxidation process is dampened above previously formed oxide. Indeed, the average height of protruding lines in region C is about 2.5 nm shorter than the height of lines passing through A and B, which corresponds exactly to the elevation of the oxide band in region C relative to the normal (unscratched) substrate. This indicates the presence of a minimal electric field necessary for the oxidation reaction to proceed since the oxidation process seems to depend purely on the distance between the substrate and the tip.

### 5.3 A more systematic study

In order to accurately describe the scratching process, it is important to know the force that is being applied. This contact force is usually calculated from a force calibration curve, such as the one shown in Fig. 5.3, that relates the cantilever deflection to the z piezo travel. The contact force is simply equal to the cantilever deflection (a - b on Fig. 5.3) multiplied by its spring constant. When there is a large change



tip#50.000

Figure 5.3: A force calibration curve showing the cantilever deflection as the tip approaches and retracts from the surface.

in the setpoint, the z-cantilever deflection is unfortunately no longer visible in the force calibration plots. However, assuming that the deflection varies linearly with the setpoint voltage, a few data points where this deflection is still visible should suffice to find the relation between both variables. A plot of cantilever deflection versus

setpoint voltage, shown below in Fig. 5.4, gave the following linear relation:

$$\Delta z = (0.47 \pm 0.07)V + (5.5 \pm 0.7).$$

Here z is the cantilever deflection and V is the setpoint voltage. Thus, changing the setpoint to +10 V from an initial value of -10 V is equivalent to an application of  $20 \pm 4$  nN.



Figure 5.4: Relation between setpoint and cantilever deflection used to calculate contact force. It was quite difficult to measure this cantilever deflection with the DI software, thus the large error bars.

Once the contact force was established, the sample was changed to 3-12-01.1. This new sample was then scratched for various lengths of time after which the resulting pit depths were recorded. As expected, the dependence is unmistakably linear, with a slope of  $0.98 \pm 0.03$  nm/minutes (Fig. 5.5). This exact value shouldn't be taken too seriously since there are many other parameters in the system that may influence the results like scan speed and contact force. It is the linearity of the scratching depths

that is important since it confirms that the tip was actually digging into the surface.



Figure 5.5: Scratch depth time dependence. Both averages parallel and perpendicular to the the fast scan direction are presented. Slope is  $0.98 \pm 0.03$  nm/minute.

At the end of each run in Fig. 5.5, oxide lines were drawn across the square with a tip bias of -15 V and writing speed of 0.1  $\mu$ m/s in order to observe the oxide characteristics at different depths (Fig. 5.6). The large deposits seen on the 10 minute trial were caused by an accidental omission of the 100 M $\Omega$  current limiting resistor in the oxidation circuit, and this error was corrected for other trials. From closeup images of the oxide lines, it was evident that the digging process was damaging the tip. The large, irregular, oxide features seen in Fig. 5.6 are a clear indications of the dulling of the AFM probe since, as seen in chapter 4, the oxide line width produced by a -15 V bias is usually about 50-70 nm. In contrast, the observed features in Fig. 5.6 are sometimes in excess of 150 nm wide. Because of this, data obtained during these experiments cannot be compared to the results from the last chapter.



Figure 5.6: Oxide lines drawn on top of scratched features. The rectangular boxes denote averaging areas used to analyze the lines.

Nevertheless, by comparing properties of the line portions inside and outside of a particular pit depth, it *is* possible to compare SPM oxide characteristics between different heterostructure layers. As seen in Fig. 5.5, a depth slightly larger than 25 nm was reached after 25 minutes of scratching. Referring to the 3-12-01.1 sample composition diagram (Fig. 5.1), this depth corresponds to the first AlGaAs layer. Any differences between the SPM oxidation of AlGaAs and GaAs should therefore turn up in the comparison of oxide lines drawn within and without of the 25 nm deep pit. This was done in Fig. 5.6 by averaging line features in the pair of boxes A and B, along with C and D, and the results are summarized in table 5.2. In general, lines written inside and outside of the scratched area seems seem to have the same height and width characteristics. The only difference is found when comparing areas C and D: in this case it looks like the oxide lines drawn on AlGaAs within the pit have a larger height than the lines drawn on the surface. Another observation that can be made from this data is that the worsening aspect ratio of the oxide lines reinforces the idea that the AFM tip loses its sharpness during the digging process.

averaging area	height (nm)	FWHM (nm)	h/w
А	$3.4\pm0.3$	$144 \pm 5$	$0.023 \pm 0.002$
В	$3.2\pm0.3$	$161 \pm 8$	$0.019\pm0.002$
С	$2.6\pm0.2$	$179 \pm 20$	$0.015 \pm 0.002$
D	$4.5\pm0.5$	$295\pm10$	$0.014 \pm 0.002$

Table 5.2: Line height results for different averaging areas in Fig. 5.6

The last scratching test made was to re-examine the effect of the large contact force on previously established SPM oxide. For this, a small 1  $\mu$ m square was oxidized by imaging the area once at a resolution of 512 lines, a voltage of -20 V and a 0.3 Hz scan frequency such that the oxide writing speed was 0.3  $\mu$ m/s. This resulted in a protruding square about 15 nm tall, shown in Fig. 5.7. Using the maximum achievable contact force of  $20 \pm 4$  nN, a larger 2  $\mu$ m square was subsequently "imaged" off for 30 minutes, resulting in the pit shown in Fig. 5.8. Even though remnants of the oxide square were still noticeable in the upper panel of Fig. 5.8, it was clear that this time, the GaAs oxide was successfully eroded away. While more tests would be needed to get the exact force at which this erosion begins, both scratching trials discussed in this chapter show that this force lies somewhere between the values of 10 and 20 nN.



Figure 5.7: Micron sized oxide square produced by writing 512 lines with a bias voltage of -20 V and writing speed of 0.3  $\mu$ m/s.

### 5.4 Summary

In this chapter, I have demonstrated that the application of large contact forces between a TiO coated silicon AFM tip and GaAs/AlGaAs heterostructures successfully scratches away the substrate surface down to any desirable depth. The linear relationship between the scratch depth and exposure time allows for specific layers in the GaAs/AlGaAs heterostructure to be uncovered, which can then be patterned by SPM oxidation. This could prove to be very useful in the fabrication of quantum devices.



Figure 5.8: substrate surface after 30 minutes of scratching. Remnants of square shown in Fig. 5.7 can be seen in upper pannel.

# 6

## Definition of a Double Quantum Dot with SPM lithography

Now that SPM nanolithography by local oxidation has been fully characterized, the steps needed to fabricate a quantum device using these lithography techniques will be discussed. In the following pages, this knowledge will be applied to the fabrication of the double quantum well shown in Fig. 6.1, while maximizing the quality of oxide lines defining the nanostructure.



Figure 6.1: Double quantum dot feature written onto a plain GaAs sample with a bias voltage of -15 V. Image size is 1.0  $\mu$ m by 1.0  $\mu$ m.

### 6.1 Sample Characterization and Contacting the 2DEG

Before being able to pattern a 2DEG heterostructure, tests must first be made in order to insure that ohmic contact of good quality are able to reach the 2DEG within the surface. To make these contacts, indium is usually diffused into the sample under the action of high temperatures, until it reaches the 2DEG. These indium contacts (see Fig. 6.2) are made by hand onto the surface of the sample, after which it is heated at high temperature such that the indium diffuses down to the 2DEG. Unfortunately, there is no universal recipe for this procedure and so a lot of trial and



Figure 6.2: Indium contacts

error experimentation must be made before the proper temperature and diffusion times are found. In my case, it was eventually found that the heat from the soldering iron sufficed to make a good contact.

Once the contacts are made, the next step consists of testing them in order to be certain that the 2DEG has successfully been reached. Usually, the quality of a contact is assessed by dipping the sample into liquid helium, after which the current-voltage (IV) trace and resistance across the connection are measured. Should the IV trace become non-linear, or should the resistance increase drastically, the contact has failed since the 2DEG is supposed to behave like a metal. For metals, resistance drops with temperature instead of rising, as it is the case for a semiconductor where resistance usually increases.

To verify the 2DEG contact quality, contacts were made using a Hall bar geometry. They were then loaded into a <sup>3</sup>He dilution fridge, cooling the sample down to 0.5 K. Measurement of the longitudinal and transversal resistance as a function of magnetic field confirmed that the 2DEG was indeed reached with the indium contacts due to observation of the integer quantum hall effect in the sample (Fig. 6.3). This effect occurs at low temperatures only for 2DEG systems where a large magnetic field is applied perpendicularly to the current flow, restricting the electrons to exist in certain quantized energy levels called Landau Levels. Consequently, for values of the magnetic field for which Landau levels are completely filled, the longitudinal resistance vanishes. The importance of this measurement is that I could be certain that the 2DEG was actually contacted. The heterostructure structure on which successful contacts were made is shown in Fig. 6.4.

### 6.2 Optical Lithography

Once the contacts were functioning correctly, the next step in the quantum device fabrication was to isolate a small area of the sample that could be patterned with the AFM. One of the main limitations of the AFM is that the scanning range is very small. In practise, drift issues limit line lengths that can be patterned with precision to about 10  $\mu$ m. To get around this issue, a first optical lithography step was needed to define a small area on which the AFM could work. For this purpose, the mask shown in Fig. 6.5 was developed.

For the optical lithography, many difference steps need to be followed. First the sample has to be coated with a thin, uniform layer of photoresist. Next, the mask



Figure 6.3: Integer quantum hall effect observed for the sample shown in Fig. 6.4.



Figure 6.4: GaAs/AlGaAs heterostructure geometry on which successful contacts were made.



Figure 6.5: Photomask design that was used to define small conductive areas on which we could draw the double quantum dot.

is placed above the sample in such a way that the desired pattern is centered upon the right spot. Then, the sample and photomask combination is irradiated with ultraviolet light which affects the photoresist in uncovered areas. This whole process is analogous to the way film captures an image in a camera. After the photoresist has "captured" the picture of the mask, it is then dipped in a developer solution that removes the exposed photoresist. In the end, we are left with a layer of photoresist on the sample having the same shape as that area originally protected by the mask (Fig. 6.6).

The last step that remains to be done before the AFM lithography, is to etch away the areas of the sample that are not protected by the resist. This will have the effect of completely removing the 2DEG except in areas that remain covered since the resist is immune to the etching solution. For this etch step, the sample was dipped for 30 seconds in a  $1:8:80 \text{ H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  solution. As a result, 200 nm of the cap layer 6: Definition of a Double Quantum Dot with SPM lithography



Figure 6.6: Protective photoresist layer remaining after the developing process.

of the heterostructure was etched away. Finally, the photoresist was removed with acetone. After this long process, the sample was now ready to be patterned with the AFM.

### 6.3 Results

Unfortunately, measurements of the electrical resistance between contacts pads of different mesas indicated that there was a strong leakage current between unconnected contact pads. This was not supposed to happen since at least 200 nm of the sample was etched-away, which was largely enough to prevent electrons from flowing between the different mesas. This unfortunate turn of events could possibly be explained by the difficulties I had in obtaining uniform photoresist coating because of the small size of the sample. For this reason, no quantum transport measurements were performed on the double quantum dot structure, even though the patterning itself was successfully completed. An image of the final product is shown in Fig. 6.7. More tests will need to be made to determine the source of the leakage between mesas and to see if it can

6: Definition of a Double Quantum Dot with SPM lithography



Figure 6.7: Final double quantum dot structure defined through AFM local oxidation. Because of drift, many steps were used in order not to accidentally cut off one of the channels.

be eliminated.

## 7

## Conclusion and Outlook

Nanolithography through local oxidation by AFM is far from an exact science. A multitude of parameters such as humidity, voltage, writing speed, tip use and sample doping can have a drastic impact on the final outcome of a lithography run. While it is unpredictable, SPM local oxidation has a very promising future because of the potential for nanopatterning with atomic precision. Of particular interest is the ability of features defined by local oxidation to deplete shallow 2DEGs allowing precise, tunable quantum structures to be fabricated with a large increase in resolution when compared to conventional e-beam and optical lithography techniques. Of great importance for the success of this technique is the quality of the SPM oxide lines. Ideally, these should be as tall as possible, while maintaining small lateral dimensions.

In this thesis, I have studied the SPM lithography process in an attempt to increase its reproducibility and optimize the quality of the resulting lines. In chapter 2, I began by reviewing the current theoretical models describing the SPM oxidation reaction. We have seen that these models are still quite simplistic and do not predict the same oxidation kinetics. Three main classes of models exist: direct logarithmic, inverse logarithmic and power law relations. In chapter 3, I describe the experimental apparatus and the modifications that were needed to be made for the SPM lithography to work. Next, I presented results concerning the characterization of the SPM oxide features. The main conclusions were that the height of oxide lines has a linear dependence on bias voltage. This corresponded very well with the Stiévenard *et al.* 's adaption of field-enhanced Cabrera and Mott oxidation theory. While Stiévenard

#### 7: Conclusion and Outlook

et al. 's model was successful in this instance, the inverse logarithmic kinetics that it predicted, on the other hand, did not fit experimental results. Instead, I found that the empirical relation proposed by Teuschler et al. most accurately describes the power law time dependence and linear voltage dependence seen in the data. Other factors governing the oxidation process, such as humidity and the type of gaseous environment, were also examined. It was seen that patterning in a controlled environment rich in oxygen and low in humidity produced the tallest lines with the best aspect ratios. In chapter 5, high contact force patterning was examined as an alternative lithography technique that could possibly be combined with SPM local oxidation to deplete 2DEGs that were normally too deep to reach by oxidation alone. Finally, in chapter 7, I described the steps necessary to define a quantum structure on a 2DEG GaAs/AlGaAs heterostructure.

Now that the SPM oxidation process has been thoroughly examined, and that the apparatus is up and running, this research should be continued by using the SPM oxidation technique to characterize the parameters affecting the depletion of 2DEGs, as well as by investigating the properties of novel quantum devices that can be defined in 2DEG GaAs/AlGaAs heterostructures. Once the writing process is mastered, the possibilities for new and interesting discoveries are endless.

### BIBLIOGRAPHY

- [1] G. Binnig and H. Rohrer, Helv. Phys. Acta. 40, 726 (1982).
- [2] D. M. Eigler and E. K. Schweizer, Nature **344**, 524 (1990).
- [3] R. Wiesendanger, Appl. Surf. Sci. 54, 271 (1992).
- [4] G. M. Shedd and P. E. Russel, Nanotechnology 1, 67 (1990).
- [5] E. E. Ehrichs, R. M. Silver, and A. L. de Lozanne, J. Vac. Sci. Technol. A 6, 540 (1988).
- [6] E. E. Ehrichs, S. Yoon, and A. L. de Lozanne, Appl. Phys. Lett. 53, 2287 (1988).
- [7] L. A. Nagahara, T. Thundat, and S. A. Lindsay, Appl. Phys. Lett. 57, 270 (1990).
- [8] J. A. Dagata et al., Appl. Phys. Lett. 56, 2001 (1990).
- [9] J. A. Dagata, W. Tseng, J. Bennett, J. Schneir, and H. H. Harary, J. Appl. Phys. 70, 3661 (1991).
- [10] S.-T. Yau, X. Zheng, and M. H. Nayfeh, Appl. Phys. Lett. 59, 2457 (1991).
- [11] N. Barniol, F. Pérez-Murano, and X. Aymerich, Appl. Phys. Lett. 61, 462 (1992).
- [12] H. Sugimura, T. Uchida, N. Kitamura, and H. Masuhara, J. Phys. Chem. 98, 4352 (1994).
- [13] P. Fay et al., J. Appl. Phys. **75** (1994).

- [14] N. Kramer, J. Jorritsma, H. Birk, and C. Schönenberger, J. Vac. Sci. Technol. B 13, 805 (1995).
- [15] P. Avouris, R. Martel, T. Hertel, and R. Sandstrom, Appl. Phys. A 66, S659 (1998).
- [16] G. Binnig and C. F. Quate, Phys. Rev. Lett. 56, 960 (1986).
- [17] H. C. Day and D. R. Allee, Appl. Phys. Lett. 62, 2691 (1993).
- [18] M. Yasutake, Y. Ejiri, and K. Saito, Jpn. J. Appl. Phys. 32, L1021 (1993).
- [19] T. Hattori, Y. Ejiri, and K. Saito, J. Vac. Sci. Technol. A 12, 2586 (1994).
- [20] E. S. Snow and P. M. Campbell, Appl. Phys. Lett. 64, 1932 (1994).
- [21] T. Teuschler, K. Mahr, S. Miyazaki, M. Hundhausen, and L. Ley, Appl. Phys. Lett. 66, 2499 (1995).
- [22] T. Teuschler, K. Mahr, S. Miyazaki, M. Hundhausen, and L. Ley, Appl. Phys. Lett. 67, 3144 (1995).
- [23] A. E. Gordon, R. T. Fayfield, D. D. Litfin, and T. K. Higman, J. Vac. Sci. Technol. B 13, 2805 (1995).
- [24] F. Pérez-Murano et al., J. Appl. Phys. 78, 6797 (1995).
- [25] J. Servat et al., J. Vac. Sci. Technol. A 14, 1208 (1996).
- [26] M. Ischii and K. Matsumoto, Jpn. J. Appl. Phys. 34, 1329 (1995).
- [27] R. Held et al., Appl. Phys. Lett. 73, 262 (1998).
- [28] R. Held et al., Appl. Phys. Lett. 73, 1134 (1999).
- [29] S. Luscher et al., Appl. Phys. Lett. 75, 2452 (1999).

- [30] T. Heinzel, R. Held, S. Lüscher, K. Ensslin, and Wegscheider, Physica E 9, 860 (2000).
- [31] T. Heinzel et al., Physica E 9, 84 (2001).
- [32] L. P. Rokhinson, D. C. Tsui, L. N. Pfeiffer, and K. W. West, Superlattices and Microstructures 32, 99 (2002).
- [33] H. Sugimura, T. Uchida, N. Kitamura, and H. Masuhara, Appl. Phys. Lett. 63, 1288 (1993).
- [34] H. Hasegawa and H. L. Hartnagel, J. Electrochem. Soc. 123, 713 (1976).
- [35] N. Cabrera and N. F. Mott, Rep. Prog. Phys. 12, 163 (1949).
- [36] D. Stiévenard, P. A. Fontaine, and E. Dubois, Appl. Phys. Lett. 70, 3272 (1997).
- [37] P. Avouris, T. Hertel, and R. Martel, Appl. Phys. Lett. 71, 285 (1997).
- [38] E. Dubois and J.-L. Budendorff, J. Appl. Phys. 87, 8148 (2000).
- [39] L. Ley, T. Teuschler, K. Mahr, S. Miyazaki, and M. Hundhausen, J. Vac. Sci. Technol. B 14, 2845 (1996).
- [40] P. A. Fontaine, E. Dubois, and D. Stiévenard, J. Appl. Phys. 81, 1776 (1998).
- [41] E. S. Snow, G. G. Jernigan, and P. M. Campbell, Appl. Phys. Lett. 76, 1782 (2000).
- [42] F. S.-S. Chien, Y. C. Chou, and T. T. Chen, J. Appl. Phys. 89, 2465 (2001).
- [43] J.-I. Shirakashi, K. Matsumoto, and M. Konagai, APA 66, S1083.
- [44] Y. Okada, S. Amano, M. Kawabe, and J. S. Harris Jr., J. Appl. Phys. 83, 7998 (1998).
- [45] Y. Matsuzaki et al., J. Cryst. Growth **201-202**, 656 (1999).

#### BIBLIOGRAPHY

- [46] D. V. Sokolov, Technical Phys. 47, 58 (2001).
- [47] I. Umezu, T. Yoshida, K. Matsumoto, and A. Sugimura, Appl. Phys. Lett. 81, 1492 (2002).
- [48] J. A. Dagata, T. Inoue, J. Itoh, and H. Yokoyama, Appl. Phys. Lett. 73, 271 (1998).
- [49] J. A. Dagata, T. Inoue, J. Itoh, K. Matsumoto, and H. Yokoyama, J. Appl. Phys. 84, 6891 (1998).
- [50] K. Morimoto, F. Pérez-Murano, and J. A. Dagata, Appl. Surf. Sci. 158, 205 (2000).
- [51] M. Lazzarino et al., Appl. Phys. Lett. 81, 2842.
- [52] H. Yokayama and T. Inoue, Thin Solid Films 242, 33 (1994).
- [53] H. Yokayama, T. Inoue, and J. Itoh, Appl. Phys. Lett. 65, 3143 (1994).
- [54] J. A. Dagata, Nanotechnology 8, A3 (1997).
- [55] T. Schmidt et al., Surf. Rev. Lett. 5, 1287 (1998).
- [56] S. Heun, T. Shmidt, B. Bessel, E. Bauer, and K. C. Prince, Synchotron Radiat. News 12, 25 (1999).
- [57] D. R. Wolters and A. T. A. Zegers-van Duynhoven, J. Appl. Phys. 65, 5126 (1989).
- [58] Y. Okada, S. Amano, M. Kawabe, B. N. Shimbo, and J. S. Harris Jr., J. Appl. Phys. 83, 1884 (1998).
- [59] Y. Okada, S. Amano, M. Kawabe, B. N. Shimbo, and J. S. Harris Jr., IEEE International Symposium on Compound Semiconductors (Institute of Physics Publishing) 156, 577 (1998).

#### BIBLIOGRAPHY

- [60] M. Calleja and R. Garcia, Appl. Phys. Lett. 76, 3427 (2000).
- [61] H. Sugimura, N. Kitamura, and H. Musuhara, Jpn. J. Appl. Phys. 33, L143 (1994).
- [62] R. Tylecote, J. Inst. Metals 78, 327 (1950).
- [63] W. Vernon, E. Calnan, C. Clews, and T. Nurse, Proc. Roy. Soc. 216A, 375 (1953).
- [64] D. Davies, U. Evans, and J. Agar, Proc. Roy. Soc. 225A, 443 (1954).
- [65] H. H. Uhlig, Acta Metall. 4, 541 (1956).
- [66] H. Torrey and C. Whitmer, Crystal Rectifiers, McGraw-Hill, 1948.
- [67] J. A. Dagata et al., Appl. Phys. Lett. 76, 2710 (2000).
- [68] R. A. Alberty and W. G. Miller, J. Chem. Phys. 26, 1231 (1957).
- [69] E. S. Snow, P. M. Campbell, and F. K. Perkins, Appl. Phys. Lett. 75, 1476 (1999).
- [70] R. García, M. Calleja, and F. Pérez-Murano, Appl. Phys. Lett. 72, 2295 (1998).
- [71] Mikromasch, Ultrasharp CSC21/TiO/50 contact silicon cantilevers.
- [72] M. Tello, F. García, and G. R., J. Appl. Phys. 92, 4075 (2002).
- [73] Y. Matsuzaki, S. Hasui, S.-Y. Kamada, A. Yamada, and M. Konagai, Jpn. J. Appl. Phys. 40, 4325 (2001).
- [74] Y. Okada, S. Amano, M. Kawabe, and J. S. Harris Jr., J. Appl. Phys. 88, 1136 (2000).
- [75] Y. Okada, Y. Iuchi, and M. Kawabe, J. Appl. Phys. 87, 8754 (2000).

- [76] R. E. Williams, Gallium Arsenide Processing Techniques, Artech House, Inc., 1 edition, 1984, Chapter 5.
- [77] P. De Wolf, J. Snauwaert, T. Clarysse, W. Vandervorst, and L. Hellemans, Appl. Phys. Lett. 66 (1995).
- [78] R. García, M. Calleja, and H. Rohrer, J. Appl. Phys. 86, 1898 (1999).
- [79] M. Calleja, M. Tello, and R. Garcia, J. Appl. Phys. 92, 5539 (2002).
- [80] N. Barniol, F. Pérez-Murano, G. Abadal, J. H. Ye, and X. Aymerich, Microelectronic Engineering 27, 27 (1995).
- [81] R. Held, T. Heinzel, P. Studerus, K. Ensslin, and M. Holland, Appl. Phys. Lett. 72, 2689 (1997).
- [82] R. Martel, private communication, 2002.
- [83] L. Tsau, D. Wang, and K. L. Wang, Appl. Phys. Lett. 64, 2133 (1994).
- [84] T. T. Tsong, Phys. Rev. B 44, 24 (1991).
- [85] W. Kern, Semiconductor International 7, 94 (1984).
- [86] J. A. Dagata, W. Tseng, J. Bennett, J. Schneir, and H. H. Harary, Appl. Phys. Lett. 59, 3288 (1991).
- [87] J. A. Dagata, W. Tseng, J. Bennett, J. Schneir, and H. H. Harary, Ultramicroscopy 42-44, 1288 (1992).
- [88] F. Pérez-Murano et al., Appl. Phys. Lett. 82, 3086 (2003).