

***In situ* x-ray standing-wave analysis of electrodeposited Cu monolayers on GaAs(001)**

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Copper was electrodeposited onto *n*- and *p*-type GaAs(001) from mMol solutions of CuSO₄ in 0.5 Mol sulfuric acid and the registration of the Cu adsorbate was analyzed with respect to the GaAs lattice *in situ* with x-ray standing waves, recording the Cu-*K*α fluorescence radiation from the sample surface while scanning the GaAs(004) Bragg reflection. For coverages below 1 ML, the determined coherent position $P_{\text{Cu}}^{004} \approx 0.0$ is in agreement with a substitutional site of the Cu. However, the coherent fraction $F^{004} \leq 0.4$ indicates that the Cu is not well ordered or occupies other sites. The measurements also show that part of the Cu diffuses a few nm into the bulk in an amount that is larger for *n* type (≈ 0.5 ML) than for *p* type (≈ 0.05 ML). If thick Cu layers are stripped at anodic potentials, the Cu desorption starts to significantly slow down at Cu coverages of about 10 ML while the anodic current stays almost constant, which is explained by the fact that the Cu film is no longer continuous. At coverages ≈ 1 ML the stripping becomes extremely slow and Cu stays at the GaAs(001) interface even while the GaAs surface dissolves, exhibiting a ‘‘reversed surfactant’’ behavior. [S0163-1829(98)03539-5]

I. INTRODUCTION

Herein is reported an *in situ* structural analysis of a semiconductor/electrolyte interface with x-ray standing waves (XSWs). Submonolayers of Cu deposited from an acidic solution of CuSO₄ at cathodic potentials adsorb predominantly in substitutional positions on the GaAs(001) electrode. Part of the Cu, about 0.5 ML for *n*-type GaAs but only ≈ 0.05 ML for *p*-type GaAs, diffuse a few nm into the bulk. At anodic potentials, the stripping of the Cu proceeds very slow and with low current efficiency, indicating a high surface affinity of the Cu.

Structural processes at semiconductor/electrolyte interfaces are poorly understood despite their importance in technical applications. Unlike the case for metal electrodes, standard electrochemical methods, which mostly rely on the measurement of charge transport to or across the interface, do not provide immediate information about surface processes for semiconductor electrodes. The limited carrier concentration in the semiconductor leads to an extended, potential-dependent space-charge region, the response of which can determine the overall current transport behavior.¹ In the case of metal electrodes, many details of structural processes such as (sub)monolayer adsorption occurring at a potential positive with respect to the Nernst potential, called underpotential deposition (UPD), or phase transition processes were already deduced from, e.g., current-voltage characteristics.²

Starting in the 1980's x-ray *in situ* measurements were employed and provided invaluable additional and detailed structural information about electrode processes for metals.

The first x-ray studies of UPD layers were performed with x-ray standing waves (XSW).^{3,4} Later, surface x-ray diffraction⁵ was successfully employed,⁶ yielding detailed information about the interface structure, the structure of adsorbates, and potential-dependent structural processes of clean metal electrode surfaces.⁷ Comparably little work has been done using semiconductor electrodes. We recently published what was to our knowledge the first *in situ* x-ray study of a semiconductor electrode, i.e., GaAs(001)/H₂SO₄ (Ref. 8) and the growth of Cu deposits.

In view of the technological importance of both the electrochemical metallization and the contamination of semiconductor surfaces by (currentless) adsorption of metal ions from solution,⁹ it is perplexing that such structures and processes have not received due attention. To the best of our knowledge, UPD phenomena and (sub)monolayer phases with higher binding energies than the bulk deposit have not been reported for semiconductor electrodes. Only a very recent *in situ* x-ray-absorption fine-structure study¹⁰ suggested that Cu is present on the GaAs surface in a nonbulklike bonding coordination at submonolayer coverages before cluster growth begins. In a voltammetric study,¹¹ it was suggested that the stability of the first Cu layer(s) may be different from the bulk. The present XSW study confirms the existence of a submonolayer Cu phase on GaAs(001) that is tightly bound to the surface, sticking surprisingly to the GaAs even when the surface is anodically dissolved/etched.

II. XSW ANALYSIS

By Bragg reflecting an x-ray plane wave from a perfect crystal, an x-ray interference field is generated inside and

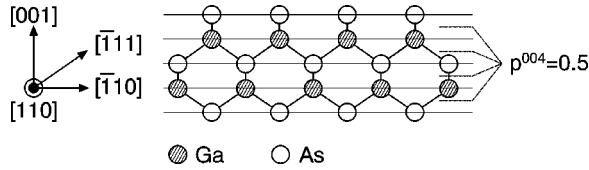


FIG. 1. A side view depicting GaAs(001). The (004) diffraction planes are indicated as well as lattice locations yielding $p^{004} = 0.5$. Cu located on the diffraction planes would give rise to $p^{004} = 0.0$.

outside of the crystal in the region of overlap between the incident and reflected x-ray beams. The planar wave field resonantly adopts the spacing of the diffraction planes. By advancing the incident angle Θ through the total reflection region, the nodal/antinodal planes of the wave field are advanced inward by one-half of a diffraction plane spacing. The range of Bragg reflection can also conveniently be traversed by tuning the energy E_γ of the incident radiation (which is accomplished by changing the Bragg angle Θ of the monochromator) as it is done in the present study. Consequently, the characteristic photoemission or subsequent x-ray fluorescence (as in the present study) of a particular atomic species will exhibit a characteristic Θ dependence, indicative of its position z_A with respect to the diffraction plane. This effect is exploited by the x-ray standing wave technique.¹²

The fluorescence intensity from an atomic species within the region of the interference field can be expressed as

$$I_F = I_0 \cdot e(\Theta) \cdot Y_F \quad (1)$$

with

$$Y_F = 1 + R(\Theta) + 2\sqrt{R(\Theta)}F^H \cos(v - 2\pi P^H). \quad (2)$$

Here, I_0 is proportional to the number of sampled atoms, i.e., the coverage; $e(\Theta) = 1$ for atoms above or in a shallow (≤ 100 nm) depth below the surface; otherwise, $e(\Theta) \ll 1$ at maximum reflectivity $R(\Theta)$ and approaches unity for $R(\Theta) \rightarrow 0$. The two parameters F^H and P^H are called coherent fraction and coherent position, respectively. If all the sampled atoms are located at the same position with respect to the diffraction planes, $P^H = z_A/d_H$ gives the position ($d_H =$ spacing of the diffraction planes) and $F^H \approx 1.0$. If the sampled atoms occupy more than one specific position with respect to the diffraction planes, $F^H < 1.0$ and P^H will represent a weighted average of the occupied positions. The parameters F^H ($0 \leq F^H \leq 1$) and P^H ($0 \leq P^H \leq 1, \text{ mod. } 1$) represent the amplitude and phase of the H th Fourier component of the distribution function of the particular sampled kind of atom, Cu in the present case.¹³ A side view of the (001) surface of GaAs crystal is depicted in Fig. 1 along with the (004) diffraction planes (i.e., $\vec{H} = [004]$). For more details on the XSW analysis, the reader is referred to the literature.^{14,15}

III. EXPERIMENT

The XSW experiments were performed at the X15A beamline at the National Synchrotron Light Source. We used a Si(004) monochromator, tuned to 10.2 keV and thus 1.2 keV above the Cu- K edge. The x-ray emission from the

sample surface was monitored by a Si(Li) solid state detector. We used the same *in situ* electrochemical cell with Pt counter electrode and Ag/AgCl reference electrode as previously employed for the *in situ* x-ray-diffraction study.⁸ All electrode potentials are quoted versus the saturated calomel electrode (SCE). We used Zn-doped (10^{19} cm^{-3}) p -type and Si-doped ($3 \times 10^{17} \text{ cm}^{-3}$) n -type GaAs crystals with (001) surface orientation. The size of the samples was 10×10 mm. The central 6×6 mm section of the specimen, which is examined by the x-ray beam, was 3 mm thick. The outer 2-mm-wide perimeter of the specimen, which was used for holding the specimen, was 1 mm thick. The crystals were etched for strain relief and the 6×6 mm surface was Syton polished.¹⁶ The samples were attached at the “wings” to the quartz holder with epoxy resin, which prevented any significant plastic distortion of the thicker, x-ray exposed central part. An Ohmic contact to the back of the samples was made by using an In/Zn solder. Prior to mounting inside the electrochemical cell, the GaAs samples were degreased with acetone and cleaned/etched by exposing them for 2 min to $\text{NH}_3/\text{H}_2\text{O}$ (1:1), 3 min to $\text{HCl}/\text{H}_2\text{O}$ (1:3), and 45 s to $\text{H}_2\text{O}_2/\text{NH}_3/\text{H}_2\text{O}$ (1:3:15), they were then rinsed with distilled water (Milli-Q) in between each of the above steps and afterwards.

After mounting the sample in the cell, a 6- μm -thick mylar window was installed and the cell was filled with 0.5 M H_2SO_4 , which had been deaerated by N_2 bubbling. With the mylar window inflated by a slight overpressure yielding a several-mm-thick sheet of electrolyte above the sample, the sample potential was cycled several times in the potential range of $-1.0\text{V} < U_S < +0.3$ V until a voltammogram indicative of a clean surface was obtained [Fig. 2(a)]; after which the H_2SO_4 electrolyte was exchanged with a solution containing CuSO_4 of defined molarity, typically 0.5 M $\text{H}_2\text{SO}_4/0.01$ mM CuSO_4 [Fig. 2(b)]. The Cu stripping peak shown in the voltammogram in Fig. 2(b) (peak labeled D) is not as sharp as might be expected since the (001) GaAs surface was not exposed to the electrolyte exclusively due to the particular shape of the specimen. For Cu deposition (and stripping), the mylar window was kept inflated and for the x-ray fluorescence and XSW measurements the window was deflated by a slight underpressure, which left a layer of electrolyte of less than 10 μm between the sample surface and mylar window.¹⁷ For p -type (n -type) GaAs samples the deposition (stripping) of Cu was performed under illumination, since the reduction (oxidation) at cathodic (anodic) potentials requires minority carriers, i.e., electrons (holes). Cu coverages were determined by comparing the Cu- $K\alpha$ fluorescence intensity (normalized by the x-ray beam intensity) from the electrodeposited samples with the Cu- $K\alpha$ fluorescence intensity from a standard sample on which a calibrated amount of Cu had been deposited in UHV. The error in the as-determined absolute coverage values is approximately 30% whereas the error in the relative values for the different preparations is approximately 15%.

A. Experimental results

In a first experiment we deposited 2400 μC at -0.64 V versus SCE on a n -type sample for which only the well-defined (001) surface, i.e., the 6×6 mm² Syton polished cen-

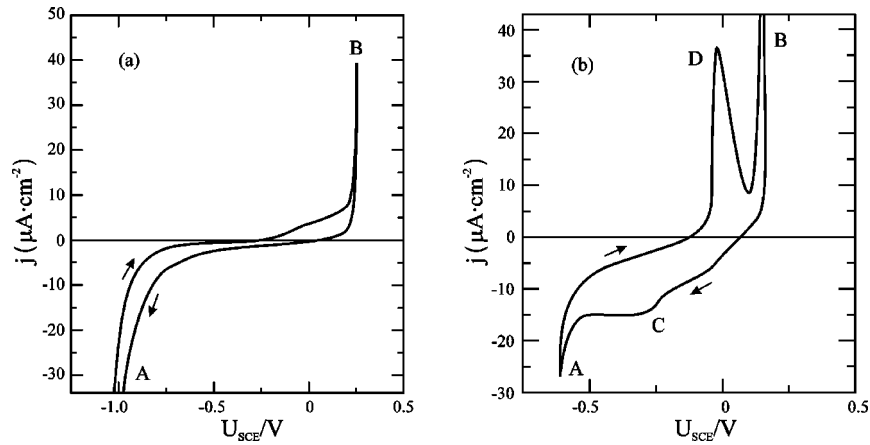


FIG. 2. Cyclic voltammogram of *p*-GaAs(001) in (a) 0.5 M H₂SO₄ (scan rate 20 mV/s) and (b) 0.5 M H₂SO₄ + 0.1 mM CuSO₄ (scan rate 5 mV/s), recorded in the electrochemical cell in thick-layer geometry. Indicated electrode currents are due to A, hydrogen evolution; B, GaAs dissolution; C, Cu deposition; and D, Cu dissolution.

tral part was exposed to the electrolyte. With a charge equivalent for Cu²⁺ of 200 μC cm⁻² per monolayer on GaAs, this deposited charge was expected to yield 33 ML of Cu. The real Cu coverage determined by the Cu fluorescence was only 9 ML, i.e., 37% of the transferred charge equivalent. This showed that coverages determined by the measured charge transfer were not reliable since part of the charge contributed to the reduction of hydrogen. In Fig. 3 the time dependency of the Cu stripping at +0.26 V is shown. For the first ML's the stripping proceeds quickly but then slows down, such that after almost 1.5 h, 0.6 ML of Cu remained on the surface.

Next we deposited Cu at -0.44 V on the same sample and stopped after a total charge transfer of 6000 μC, which should correspond to 83 ML Cu if all the charge would have been used for the reduction of Cu²⁺. However, similar to the previous case, with x-ray fluorescence we detected only 22 ML of Cu, i.e., 27% of the charge equivalent, on the surface. Figure 4 shows the stripping of this Cu coverage performed at +0.36 V versus SCE. Plotted is the Cu coverage measured by fluorescence versus the charge transfer per unit area measured by the electrode current. As one can see, for the first 10 ML stripped, the reduction in coverage measured by the Cu fluorescence and the coverage equivalent determined by the transferred charge are equivalent to within 10%, i.e., within the limits of error the current efficiency was close to unity

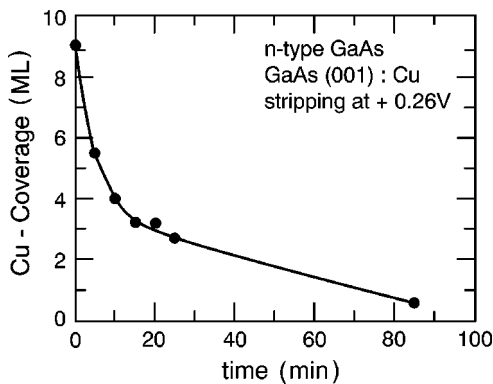
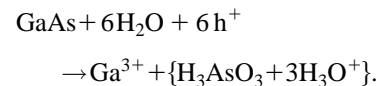


FIG. 3. Time dependence of the stripping of Cu at +0.26 V vs SCE.

for the dissolution (oxidation) of the Cu. However, with further decreasing Cu coverage, a strongly decreasing fraction of the totally transferred charge is utilized for the dissolution of the Cu. Two distinct changes in the slope of the stripping curve can be identified at ≈10 ML and at ≲2 ML Cu coverage. This behavior of the stripping of Cu was found to be the same for *n*- and *p*-type samples. During the stripping process, the anodic current dropped from initially 2.8 μA cm⁻² to 1.9 μA cm⁻².

We investigated the anodic stripping behavior of Cu at low Cu coverage in more detail. The anodic current in the electrolytic cell that is not consumed by the stripping of copper is due to the dissolution of GaAs according to the reaction¹⁸



Thus, 300 μC cm⁻² are needed to dissolve one layer of Ga or As, i.e., to remove a layer of 0.141 nm thickness. We

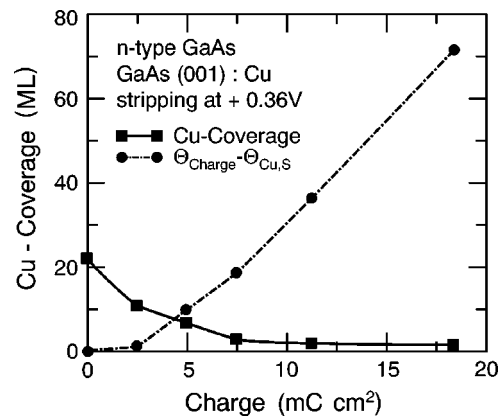


FIG. 4. Stripping of Cu., i.e., Cu coverage as determined by x-ray fluorescence versus anodic charge at an anodic potential of +0.36 V vs SCE. Shown is also the Cu-charge equivalent (Θ_{charge}), i.e., the Cu which would have been stripped if all the measured anodic charge would have been due to dissolution of the Cu, minus the real stripped Cu ($\Theta_{\text{Cu,s}}$) as determined by the Cu-K_α fluorescence.

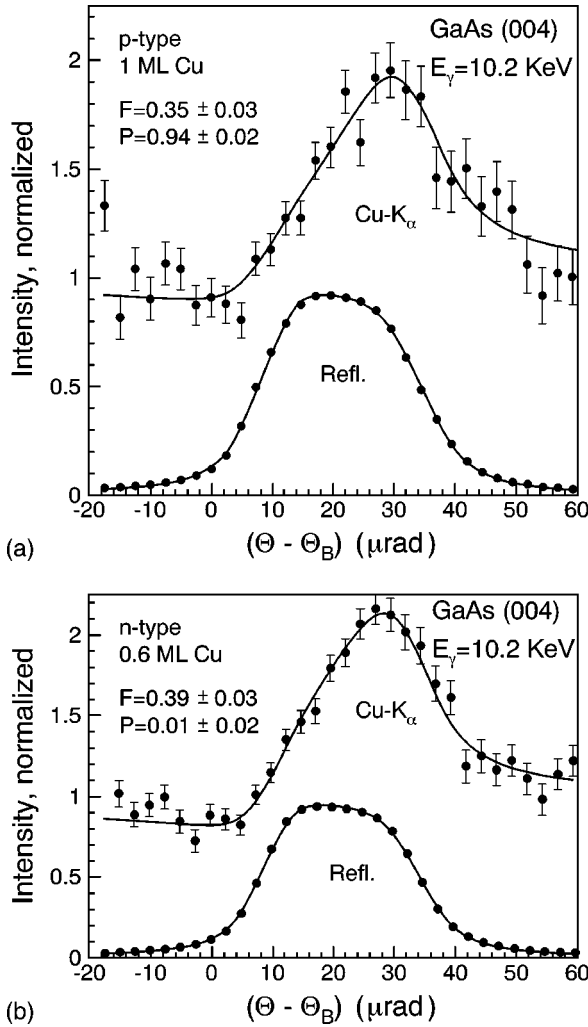


FIG. 5. The results of two *in situ* x-ray standing wave measurements for Cu electrodeposited on (a) *p*-type and (b) *n*-type GaAs(001).

investigated the removal of Cu upon extended anodic oxidation of the GaAs. The results of three different experiments starting at Cu coverages of about 1 ML or less are shown in Table I. The last experiment shows that even after removing almost 10 nm of the crystal surface, less than 1/2 ML Cu is stripped away.

We used the XSW technique to investigate the lattice location of Cu for Cu coverages of 1 ML or less on *n*- and *p*-type samples. The Cu coverages were adjusted by depositing coverages larger than 1 ML followed by a subsequent stripping. Two results for a *p*- and a *n*-type sample are shown in Fig. 5. For the whole set of measurements, the P values showed some scatter [$P \approx 0.95$ to $P \approx 0.1$ (mod. 1)], which was significantly larger than the statistic error ($\Delta P \approx 0.02$). There was no identifiable P value dependency on the dopant type. The average P value from all (11) preparations is $\langle P \rangle = 0.03 \pm 0.04$, i.e., very close to the P -value expected for a substitutional site (at a Ga or As position) for the Cu. However, the coherent fractions F never exceeded a value of 0.4 and decreased for Cu coverages exceeding ≈ 1 ML. For a preparation of 0.6 ML Cu on *n* type, we performed two XSW measurements at potentials of +0.46 V and -0.44 V versus SCE that, however, yielded the same P value.

TABLE I. Anodic dissolution of GaAs and stripping of Cu at a potential of +0.26 V vs SCE $\Theta_{\text{Cu},i}$ =initial Cu coverage; t_s =dissolved GaAs thickness determined from the anodic charge (current \times time); $\Theta_{\text{Cu},f}$ =final Cu coverage; $\Theta_{\text{Cu},s}$ =stripped Cu coverage.

Type	$\Theta_{\text{Cu},i}$ [ML]	t_s [nm]	$\Theta_{\text{Cu},f}$ [ML]	$\Theta_{\text{Cu},s}$ [ML]
<i>p</i>	0.63	2.4	0.53	0.1
<i>n</i>	1.06	4.7	0.60	0.46
<i>p</i>	1.04	9.4	0.64	0.40

A *p*-type sample that had yielded $F=0.35$ for the *in situ* measurements was exposed to air by draining the electrolyte and removing the mylar window and then measured again with XSW. The result obtained within 2 h after air exposure gave a coherent fraction of $F=0.05 \pm 0.04$, i.e., close to zero within the limits of error. The same experiment was performed with a *n*-type sample covered with 1.3 ML Cu and for which the analysis showed $F=0.27$ for the *in situ* measurement. The XSW measurement was performed within 3 h after air exposure. The result of the measurement yielded an F value that had decreased only by 26% to $F=0.20 \pm 0.02$, i.e., *n*-type and *p*-type samples behaved differently.

IV. DISCUSSION OF RESULTS

Draining the electrolyte and removing the mylar window, the GaAs surface is exposed to air and will oxidize. The oxide formation has been investigated by Lukes¹⁹ and shows a logarithmic time dependency. After three hours a thickness of 2 nm is reached (which increases to about 4 nm within two years). The decrease in coherent fraction, i.e., the disordering of the Cu layer after air exposure must be attributed to the surface oxidation. This proves that for the *p*-type samples the deposited Cu is located on the surface or within a depth of less than 2 nm and only a small fraction (≈ 0.05 ML) may have diffused deeper into the bulk. For the *n*-type sample the coherent fraction of the 1.3 ML Cu decreases only by 26% after air exposure proving that ≈ 1 ML of Cu had diffused deeper than 2 nm into the GaAs crystal. These seemingly controversial results for *p*- and *n*-type GaAs are actually supported by the literature. The solubility of Cu in GaAs was found to be dependent on dopant type and concentration.²⁰

The XSW results in terms of P and F did not show any significant difference between Cu on *n*- or *p*-type samples.

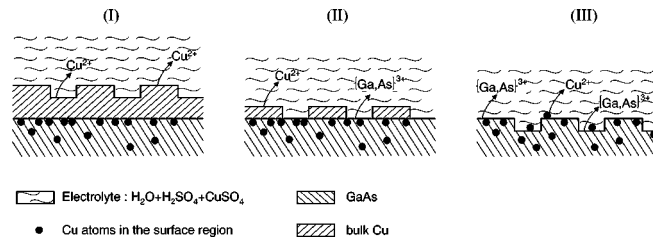


FIG. 6. Schematic illustration of the stripping behavior of Cu on GaAs(001): (I) The continuous film of Cu is dissolved; (II) Islands of Cu are left that are going into solution together with GaAs; (III) Cu left in the surface region is slowly dissolved, the majority of the anodic current is due to the stripping of GaAs.

The average P value $\langle P \rangle = 0.03 \pm 0.04$ suggests that the Cu is basically occupying substitutional sites, but the F values smaller than 0.4 prove that a significant fraction of the Cu is either disordered or located on (several) other sites distributed around the mean, substitutional location. Copper in GaAs is known to reside in a number of different defect sites²¹ with the substitutional position being the dominant lattice location.²⁰ Thus, a P value of 0.0 and a value of $F \ll 1.0$ is expected for Cu in the bulk of GaAs. However, our results show that for p -type samples, where the Cu is within 2 nm of the surface, and for n -type samples, where the majority of the Cu has diffused deeper, the P - and F -values are alike. In our opinion this proves that also in case of the p -type GaAs the Cu is not really located *on top* of the (001) surface since the surface Cu would exhibit a different bonding geometry and this would most probably lead to a change in the resulting (measured) P and/or F value. We believe that even for the p -type samples all of the Cu is located within the top surface layer(s). This assignment is also supported by the stripping behavior of Cu, which we will discuss next.

For thick Cu layers ($\Theta_{\text{Cu}} > 10$ ML) all the anodic charge is consumed by stripping the Cu. As Fig. 3 shows, the decrease in Cu coverage and the increase in anodic charge are equivalent. At a Cu coverage of about 10 ML this situation changes; the amount of stripped Cu becomes smaller than the determined anodic charge equivalent. This can be explained by the fact that the Cu film becomes discontinuous. While part of the anodic charge is consumed by stripping the Cu islands, an increasing fraction of the total anodic charge is consumed by GaAs going into solution. Eventually the bulk-like Cu islands are dissolved, ≤ 2 ML Cu are left (within the surface region) and the Cu stripping rate exhibits another strong decrease. The surface of the GaAs is etched away but Cu is removed very slowly. The anodic desorption behavior of Cu is schematically illustrated in Fig. 5. In Table I we can see that ≈ 5 nm of the GaAs surface needs to be removed for n type to decrease a ML of Cu by $\approx 50\%$. This is consistent with the results from the oxidation experiment from which we concluded that $\approx 25\%$ of the monolayer Cu coverage was at a depth of ≤ 2 nm. However, Table I seems to suggest that for a p -type sample the Cu is at a *larger* depth since larger amounts of the GaAs have to be dissolved to remove the Cu. However, this is in contrast to the oxidation experiment from which we concluded that $\approx 90\%$ of the Cu is at a depth ≤ 2 nm. The only explanation for this discrepancy is that the majority of the Cu stays at or below the surface while it is slowly etched away. I.e., the Cu behaves like an inverted surfactant on p -type GaAs(001). It is clear that the binding energy of the Cu to the GaAs at or close to the surface must be high.

The presented results of the XSW measurements do not indicate the formation of a well-ordered ML or sub-ML phase of Cu with an unique adsorption site on the GaAs(001) surface. Deposited in UHV, ML coverages of metals on

clean semiconductor surfaces frequently form ordered adsorbates or two-dimensional alloys at ML coverages. In most other cases the metal adsorption leads immediately to the nucleation of bulk alloy phases. However, the adsorption of Cu on GaAs(001) shows also in UHV a strange behavior; no ordered ML phase is formed and no alloy formation seems to occur. On the As-rich surface, up to ≈ 0.5 ML of Cu is imbedded seemingly in a disordered surface, destroying the GaAs(001)-(2 \times 4) reconstruction, and Cu clusters grow at higher Cu coverage.²² Thus, the Cu adsorption from the electrolyte and in UHV does basically seem to behave similar. Only the amount of Cu adsorbed within the surface region is higher in the case of electrodeposition. One reason for this is the larger surface roughness of the GaAs(001) surface in the electrolyte.⁸ Whether this is the only reason or whether other mechanisms lead to higher adsorption or absorption of the Cu cannot be determined at present.

V. CONCLUSIONS

Our *in situ* XSW measurements of Cu electrodeposited on GaAs(001) from acidic solutions of copper sulfate show that ML amounts of Cu are imbedded in the (001) surface (region) (see Fig. 6). Our results show that most of the Cu is occupying positions on the (004) diffraction planes ($P^{004} \approx 0.03$), possibly substituting for Ga (or As), but that unavoidably Cu also adsorbs/absorbs at other lattice locations or is disordered, since coherent fractions never exceeded a value of 0.4. Cu diffuses a few nm into the bulk of the GaAs in an amount that is larger for n than for p type. Particularly for p -type samples, the Cu is stripped at an extremely slow rate, and Cu remains at the surface while the GaAs is anodically dissolved.

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