Electrochemical growth of copper on well-defined $n$-Si(111):H surfaces

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Received 16 July 2004; accepted for publication 24 November 2004
Available online 14 December 2004

Abstract

Monohydride-terminated $n$-Si(111) electrodes were used as substrates for the electrodeposition of Cu from 0.1 M H$_2$SO$_4$ + 0.1 mM CuSO$_4$. In situ scanning tunneling microscopy, ex situ atomic force microscopy and scanning electron microscopy revealed that (a) the nucleation starts preferentially at surface defects such as etch pits or step edges, and (b) the deposition occurs by a Volmer–Weber growth mode. In situ surface X-ray diffraction on this system, reported for the first time, revealed the structure and the epitaxial relationship of the copper deposit on the Si substrate. Under the X-ray beam, the Cu deposit could be stabilized only with a significant overpotential. Cu clusters grow with the (111), (110), and (001) planes oriented parallel to the Si(111), with the first two orientations being dominant. Within the Si(111) plane, Cu clusters can be found in any rotational orientation around the Si(111) surface normal. The intensity distribution can be described as powder rings. This distribution is, however, peaked along specific directions. For the Cu clusters with Cu(110)||Si(111) it is found that in-plane Cu(111)||Si(110). The peaks in the distribution of the Cu clusters with Cu(111)||Si(111) reveal that these Cu clusters are basically rotated by 30° around the Si(111) surface normal but exhibit additionally a ±4.5° epitaxial rotation around the mean, high symmetry direction.

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Keywords: Atomic force microscopy; Electrochemical methods; Scanning tunneling microscopy; X-ray scattering, diffraction, and reflection; Copper; Silicon; Low index single crystal surfaces; Growth

1. Introduction

The metallization of semiconductor surfaces is still mostly performed in vacuum by evaporation or sputtering. The process itself is of great technological importance for the formation of Schottky
barriers and ohmic contacts in electronic devices. As an alternative to the deposition from the vapor phase, many metals can be electrodeposited onto semiconductors from solution. By varying the overpotential or the composition of the electrolyte, it is possible to influence the growth mode and the structure of the deposit. Therefore it is necessary to understand in detail the mechanisms of nucleation and growth as well as the structural properties of electrodeposits.

Because of a replacement of aluminum by copper in the silicon metallization process [1], the electrochemical deposition of metals, particularly of copper, on silicon has received increased interest in recent years. Despite its great industrial importance, relatively little work is reported in the literature on the fundamental aspects of electroplating on semiconductor substrates [2–12]. So far, most of the work about metal deposition onto semiconductors was performed with classical electrochemical methods, whereas modern structure-sensitive techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) or surface X-ray diffraction (SXRD) are not widespread in use.

In the following, we report on the electrochemical copper deposition onto H-terminated n-Si(111) from 0.1 M H₂SO₄ + 0.1 mM CuSO₄, using classical electrochemical methods and surface science techniques for structure analysis (STM, AFM, SXRD) in order to gain a better insight into the initial stages of Cu deposition on n-Si(111):H, the growth mode of the deposit, and its structural and epitaxial properties.

### 2. Experimental

#### 2.1. Substrate preparation

One-sided polished n-Si(111) samples, phosphorus-doped, 1–20 Ω cm ($N_D = 10^{15}$ cm$^{-3}$) with a miscut angle of about 0.1° were used (except for the SXRD study supplied by Wacker Siltronic AG, Burghausen, Germany). They were cleaned following the RCA cleaning procedure [13], which means degreasing in 2-propanol under reflux for 2 h and then boiling alternating for 15 min in basic and acidic H₂O₂ solutions (NH₃:H₂O₂: H₂O = 1:1:5 and HCl:H₂O₂:H₂O = 1:1:5). Prior to each experiment the samples were etched for 1 min in 50% HF (Merck, VLSI Selectipur) to remove the oxide layer and for 3 min in 40% NH₄F (Merck, VLSI Selectipur). This last step is known to result in well-defined, monohydrid-terminated Si(111) [Si(1 11):H] surfaces with large, atomically flat terraces [14–16]. Ohmic contacts were formed by applying an In/Ga eutectic alloy on the back of the wafers after the etching procedure.

#### 2.2. Electrochemical deposition of copper on n-Si(111):H

Copper was deposited from 0.1 M H₂SO₄ + $10^{-4}$ M CuSO₄ prepared from CuSO₄ (Merck, puriss p.a.), H₂SO₄ (Merck, suprapure) and ultra pure water (18.2 MΩ cm, TOC < 2 ppb). The electrochemical experiments were performed in the dark in a conventional three-electrode glass cell connected to a potentiostat. A saturated calomel electrode (SCE) and a platinum wire served as reference and counter electrode, respectively. All potentials are reported versus SCE.

#### 2.3. Scanning probe microscopy

The morphology of the deposited copper was characterized in situ by STM (Topometrix TMX 2010 Discoverer, USA), and ex situ by contact mode AFM (Molecular Imaging, Tempe, USA), the latter operating in air and with silicon cantilevers (spring constant 0.26 N m$^{-1}$, Park Scientific Instruments, USA). The samples for AFM were prepared in a standard electrochemical cell immediately before imaging.

#### 2.4. Surface X-ray diffraction (SXRD)

SXRD experiments were performed at the beamline ID32 at ESRF (Grenoble, France) using a photon energy of 8.8 keV ($\lambda = 1.41$ Å). Data were recorded in specular geometry and in grazing incidence geometry, scanning along the high sym-
metry in-plane directions of the silicon substrate using a so-called 2 + 2, four-circle diffractometer.

The principle of the electrochemical cell used for the in situ structural characterization of metal deposits has been described elsewhere [8,17]. An important improvement of the already existing cell design [8] was the omission of polyamide screws and the replacement of Viton® O-rings by Kalrez® rings in the sample holder (see Fig. 1) to avoid contaminations, since polyamide and Viton® cannot be cleaned in Caro’s acid (H₂O₂ + H₂SO₄). The cell itself was made of Kel-F. The crystals used in this cell had the shape of a hat, such that the surface is freely accessible to the X-ray beam even at grazing incidence. The electrochemical SXRD cell was equipped with a miniaturized Ag/AgCl reference electrode and a Pt ring as a counter electrode.

For the SXRD measurements a charge equivalent of about 20 monolayer of Cu was deposited at various overpotentials, where a monolayer amount is defined here by a densely-packed Cu layer. The deposition was carried out in the so-called ‘thick-layer geometry’, i.e., with the Mylar window inflated by a slight liquid overpressure. The X-ray measurements were performed in the ‘thin-layer geometry’ [17], i.e., with the Mylar foil sucked against the sample surface by a slight underpressure, leaving just a few μm of electrolyte on the surface. It was found that the Cu deposit desorbed under the X-ray beam [18]. Whereas deposition commenced at −500 mV vs. SCE, during the X-ray illumination the potential had to be adjusted at −650 mV vs. SCE, which is already within the range of H₂ evolution, in order to stabilize the Cu deposit. The results presented here have been obtained in situ but some samples have been studied ex situ as well.

3. Results

3.1. Electrochemical deposition of Cu onto n-Si(111):H

The inset of Fig. 2 shows a typical cyclic voltammogram for copper deposition onto n-Si(111):H, which starts at about −0.5 V. This is about 0.5 V more negative than the equilibrium potential for Cu²⁺/Cu in that electrolyte, and about 0.2 V more negative than the flat-band potential E_FB. There is no indication for underpotential deposition. The voltammogram is characterized by a deposition peak at −0.55 V, and the onset of hydrogen evolution at about −0.6 V. On the reverse scan no stripping peak can be observed as copper on silicon forms a Schottky junction [19]. These results are consistent with those obtained earlier by Ji et al. [9] and Zambelli et al. [10].

In order to examine the nucleation mechanism of Cu on n-Si(111):H, potential step experiments in the dark were performed. The starting potential for all current transients was −0.1 V, i.e., positive
of the flat-band potential, and the final potential varied from \(-0.52\, \text{V}\), close to the onset of Cu deposition, up to \(-0.68\, \text{V}\), where hydrogen evolution on the deposited Cu takes place. Fig. 2 shows the resulting current transients, which are all characterized by a rising part, indicating a nucleation-and-growth mechanism, followed by a current decay due to diffusion limitation. In this range the Cottrell equation is valid \([20]\). The current transients were analyzed according to the nucleation-and-growth model of Scharifker and Hills for three-dimensional nucleation and growth under diffusion control \([20,21]\), which allows for a classification into instantaneous and progressive nucleation. For instantaneous nucleation the rate law is given by \([20]\):

\[
I(t) = \frac{z \cdot F \cdot D^{1/2} \cdot c_0}{\pi^{1/2} \cdot t^{1/2}} \times \left[ 1 - \exp \left( -N_0 \cdot D \cdot (8\pi^3 c_0 V_m)^{1/2} \cdot t \right) \right]
\]

(1)

with \(c_0\) being the bulk concentration of the metal ion, \(V_m\) the molar volume and \(D\) the diffusion coefficient. \(N_0\) is the number of nucleation sites. In the case of progressive nucleation the corresponding rate law is given by \([20]\):

\[
I(t) = \frac{z \cdot F \cdot D^{1/2} \cdot c_0}{\pi^{1/2} \cdot t^{1/2}} \times \left[ 1 - \exp \left( -\frac{2}{3} k_n N_0 \cdot D \cdot \left(8\pi^3 c_0 V_m\right)^{1/2} \cdot t^2 \right) \right]
\]

(2)

with \(k_n\) being a rate constant for nucleation.

It is common practice to plot the transients in a normalized form, \((I/I_{\text{max}})^2\) vs. \((t/t_{\text{max}})\), where \(I_{\text{max}}\) is the maximum current of the transient and \(t_{\text{max}}\) the time at which the current reaches its maximum \([20]\). The experimental transients can then easily be compared with the theoretical ones. Such a plot is shown in Fig. 3 for one transient. The experimental data fit neither the progressive nor the instantaneous nucleation model, although there is a strong indication for progressive nucleation. Other groups have also suggested a progressive nucleation from their experiments \([9,22]\).

As the Cottrell equation is valid for the falling part of the transient, one can derive the diffusion coefficient from the curves in Fig. 2. A mean value for \(D(\text{Cu}^{2+})\) of about \(1.2 \times 10^{-5}\, \text{cm}^2\, \text{s}^{-1}\) is obtained, which is in good agreement with values found in the literature \([6]\).
To substantiate our conclusions about the nucleation mechanism, scanning electron microscopy (SEM) images of Cu deposited onto $n$-Si(111):H were recorded (Fig. 4). These images clearly show Cu crystallites of different sizes on the surface, which points directly to progressive nucleation [9,22]. The cluster cover about 19% of the surface from which value an average cluster height of 11 nm can be deduced.

3.2. Scanning probe microscopy

The early stages of copper electrodeposition were also studied by in situ STM and ex situ AFM. For the STM experiments copper was deposited during a short potential step with the STM tip far retracted from the surface. Recent investigations of metal deposition on $n$-Si(111):H revealed difficulties with in situ STM for imaging the metal-covered semiconductor surface, because of a rather positive tip potential required for imaging the Si surface [23–25]. Thus, the positively charged metal ions are electrostatically repelled and no metal deposition takes place under the tip. This happens also in the case of copper, but deposition is possible if the STM tip is retracted far enough from the surface. Imaging of the metal clusters after deposition is then possible without inducing changes in the surface morphology. Once deposited, a fast reaction between Cu and Si takes place, removing the H-termination and creating very strong Cu–Si bonds [26].

For the AFM measurements the metal was deposited in an electrochemical cell. Immediately afterwards the sample was transferred to the microscope and imaged in air (Fig. 5).

In all cases the typical step structure of H-terminated $n$-Si(111) as well as small crystallites (white spots) of deposited Cu are visible. The appearance of metal clusters suggests a purely three-dimensional growth (Volmer–Weber growth mode), which is consistent with results obtained both in electrolyte and in UHV, for Cu on a $n$-Si(111):H surface [9,10,27–29]. At first glance it seems that there is no preferential nucleation site on the surface. A closer look, however, reveals that most of the metal particles have nucleated at surface defects (see white arrows in Fig. 5). Only very few do not seem to being accompanied by defects (white circles). Other groups reported the same observations, showing a defect-induced nucleation even more clearly [10,29]. However, Zambelli et al. and Homma et al. used $n$-Si(111):H samples which were etched in deoxygenated NH$_4$F solution to avoid any formation of etch pits while we used oxygen-containing NH$_4$F solution [29–33]. As a consequence, the only defects on the surfaces prepared in O$_2$-free NH$_4$F are steps, at the edges of which the copper clusters nucleate. In our case, surface defects are created also on the terraces during the etching in O$_2$-containing NH$_4$F; and hence, deposition takes place not only at step edges but also on terraces, which can be seen clearly in Fig. 5a and c.

3.3. X-ray investigations

A closer look at the SEM images in Fig. 4 reveals that most of the Cu crystallites exhibit a
triangular or hexagonal shape and only very few are of square- or rectangular-like shape. The edges of most of the clusters appear to be aligned along preferential directions. Thus, the clusters are reflecting the symmetry of the substrate surface. This seems to suggest that Cu is growing mostly with its (111) planes parallel to Si(111) and that the crystallites are in-plane epitaxially aligned with the substrate.

For testing these assumptions and for quantitatively characterizing the epitaxial properties of the system, an in situ X-ray diffraction (XRD) analysis of electrochemically deposited copper on n-Si(111):H was performed at the beamline ID32 at the ESRF (Grenoble, France). To describe the reciprocal lattice, we adopt a hexagonal surface coordinate system for the Si substrate ($a_{Si} = 5.431 \text{ Å}$) with the reciprocal lattice vectors $a^*$, $b^*$, $c^*$, where $\gamma(a^*, b^*) = 60^\circ$ and $\beta(a^*, c^*) = \alpha(b^*, c^*) = 90^\circ$, $|a^*| = |b^*| = 1.8892 \text{ Å}^{-1}$, and $|c^*| = 2.004 \text{ Å}^{-1}$.

A charge equivalent of about 20 monolayer of Cu was deposited from a solution of 0.1 M H$_2$SO$_4$ + 0.1 mM CuSO$_4$ onto the sample. The resulting specular $\Theta$-, 2$\Theta$-scan, i.e. the $q$-scan along the [00$l$]$_{hex}$ direction of Si, is shown in Fig. 6a. Four peaks can be distinguished: one for Cu(111), one for Cu(200), a broad peak at around 3.7 Å$^{-1}$ caused by the Mylar foil used for covering the in situ SXRD cell, and a sharp spike from the “forbidden” Si(222) reflection at about
From the intensity distribution of the peaks it is obvious that the fraction of Cu, which grows preferentially with its (111) planes parallel to the Si(111) plane, is about 10 times larger than the fraction, which grows with its (001) planes on the Si(111) surface, consistent with the assumption based on the SEM images. The small peak from Cu(200) would explain the occasional appearance of rectangular shaped crystallites. In contrast, for an investigation of Cu UHV deposition onto Si(111):H, Demczyk et al. found a signal only for Cu(111) in the specular scans [34].

The $q$ values of all peaks in the specular scan correspond within experimental error to the $q$ values for fcc Cu; therefore the crystallites are unstrained. The exact experimental values for $q$ and $\Delta q$ (taken from higher-resolved scans for each peak) as well as the theoretical values for fcc Cu are summarized in Table 1. The average thickness of the crystallites can be estimated by $N_{111} = q_{111}/\Delta q_{111} = 135$, where $N_{111}$ is the number of (111) planes in the crystallite, yielding a height of about 28 nm, which agrees roughly with the ex situ SEM observation, where a height of about 11 nm was found after depositing 10 ML Cu. From the FWHM of $\theta$-scans for each peak (Fig. 6b) one can deduce information on the mosaic spread of the Cu crystallites. These results are also listed in Table 1.

To gain information about the in-plane epitaxial order of the Cu deposit with respect to the substrate, in-plane scans at grazing incidence (scans in the $h$–$k$-plane at small $l = \delta \approx 0.1$) were performed.

### Table 1

| Parameters of the Cu peaks which had been identified in the specular scan (cf. Fig. 6) |
|-----------------|-----------------|-----------------|-----------------|
| $q/\text{Å}^{-1}$ | $\Delta q/\text{Å}^{-1}$ | $q_{\text{bulk-Cu}}/\text{Å}^{-1}$ | $\Delta \theta$/deg (mosaic spread) |
| Cu(111)         | 3.0065           | 0.0222           | 3.0063          | 0.41 |
| Cu(200)         | 3.4689           | 0.0291           | 3.4714          | 0.69 |

Fig. 6. (a) Specular $q$-scan along the [001] direction of Si after deposition of about 20 monolayer of Cu at $E_{\text{sample}} = -550 \text{mV vs. SCE}$. (b) $\theta$-scans at Cu(111) and Cu(200), showing the mosaic spread of the deposit.
For the in-plane scan we expect to identify peaks from lattice planes of the Cu which are normal to the Cu(111) planes, e.g., Cu(220) and Cu(211), and peaks from diffraction planes which are normal to Cu(200), e.g., Cu(002) and Cu(022). The result for the scan along the \( h0d \)_hex direction (\( h \)-axis of the Si substrate) is shown in Fig. 7a. Two peaks can be distinguished: One corresponding to Cu(111) and one to the Cu(220) lattice spacing.

The observation of the Cu(111) in-plane peak means that the Cu also grows with crystal orientations parallel to Si(111) other than (111) and (100), the two orientations which had been observed in the specular scan. A likely candidate is the low index plane Cu(110) since e.g. the Cu(−110) is normal to Cu(111). \(^1\) The SEM images in Fig. 4 also show crystallites with a more rectangular shape, which points to (110) Cu planes parallel to Si(111).

The Cu(002)/(020) peaks, coming from the Cu planes which are normal to Cu(100), which had been identified in the specular scan, are hardly detectable in the in-plane scan. Only a very small hump characteristic of Cu(002)/(020) at \( h = 1.84 \) can be observed in Fig. 7 between the Cu(111) peak at \( h = 1.6 \) and the sharp Si(222) spike at \( h = 2 \).

Information on the in-plane orientation and mosaicity of the Cu crystallites can be deduced from grazing incidence in-plane \( \omega \)-scans at \( |q| = |q_{hkl}| = \text{const} \) for the different \( q \)-values of each in-plane peak (Fig. 7b and c). As a subset of the \{110\} planes, i.e., \{−110\}, \{1−10\}, and \{−101\}, lie perpendicular to the (111) plane, as explained above, the position and shape of the peaks provide information about the preferred rotation of the (111) oriented Cu-clusters within the Si(111) plane. [Note, however, that two of the family of \{110\} planes are also perpendicular to the (100)

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\(^1\) The in-plane detected Cu(111) peak could in principle also arise from Cu(211) planes growing parallel to Si(111), since, e.g., Cu(−211) is normal to Cu(111), and from other higher-order lattice/diffraction planes.
plane, i.e., (0 1 1) and (0 −1 1)]. The ω-scan around the in-plane Cu(220) is shown in Fig. 7b. One can see peak-doublets with a separation of Δω = 60°, reflecting the sixfold symmetry which is expected for a Cu(111) layer, and which shows again that the (111) plane of the Cu fcc lattice is preferentially aligned with the (111) plane of the fcc lattice of silicon.

However, a splitting of the Cu(220) peaks shows that the Cu lattice is in-plane epitaxially rotated by ±4.5° around the high-symmetry mean direction. The center of the peak doublets is oriented in-plane toward the h 1 0 i direction of Si (in hexagonal coordinates), which means, that the mean orientation of the (111) plane of the Cu clusters is rotated in-plane by 30° with respect to the Si(111) plane. This was also observed for Cu clusters deposited in UHV on Si(111):H [34], however, without the additional ±4.5° epitaxial rotation.

The ω-scan on the in-plane Cu(111) peak, which arises from the Cu clusters with Cu(110)[Si(111)], shows also maxima at selected ω-values (Fig. 7c) in 60° intervals pointing toward epitaxial alignment. The peaks occur exactly at the hexagonal in-plane (11) direction of the Si substrate, which means that {111} planes of these clusters are parallel to Si{110} planes.

The peaked intensity distribution shows that the Cu clusters grown on Si(111):H exhibit a preferred in-plane orientation with respect to the substrate lattice. However, from Fig. 7a it can be seen that the background level at the Cu(111) peak is at around 600 a.u. and the background level at the (220) peak is around 300 a.u., whereas the signal level in the ω-scans is above 700 in the former and above 400 in the latter case at any ω-value. This means that while the in-plane orientation distribution of the Cu clusters is clearly peaked, with a sixfold symmetric in-plane peak-distribution, clusters can also be found at any in-plane orientation, forming a powder ring. This was also confirmed by radial scans (not shown here), which revealed Cu peaks at any ω-position, proving the above said.

There seem to be some additional fine structure in the ω-scans, suggesting that some other in-plane orientation directions, other than the high-symmetry directions, are preferred by the clusters. Similar observations had been made for UHV deposited Cu on Si(111), where the epitaxy was, however, limited to Cu(111)[Si(111)] [34].

4. Conclusions

The electrodeposition copper onto atomically flat n-Si(111):H surfaces is an irreversible process due to the formation of a Schottky-barrier at the Cu/Si-interface. The nucleation process can be characterized as progressive, which is concluded from in situ STM, ex situ AFM and SEM images. Nucleation starts preferentially at surface defects, such as etch pits or step edges. The deposition proceeds on Si(111):H in a pure Volmer–Weber growth mode, as STM and AFM images suggest.

This is confirmed by in situ SXRD experiments. They furthermore show that the Cu clusters grow epitaxially with the Cu(111) planes and (110) planes predominantly aligned parallel to the Si(111) planes. A fraction of clusters, less than 10%, grows with the (100) planes parallel to Si(111). The out-of-plane mosaicity of the Cu clusters is small, less than 0.5°, i.e., the corresponding Cu planes are well aligned parallel with the Si(111) surface plane.

The q-values of the Cu peaks obtained from the specular scans are in good agreement with the bulk lattice constants of fcc copper, which means that there can be only very little strain in the crystallites.

The in-plane mosaicity is large and Cu clusters can be found in any orientation. However, the orientation distribution of the Cu clusters is clearly peaked along preferred, directions of Si(111) surface. The (111) planes of the Cu clusters, which are parallel to Si(111), are epitaxially rotated. The peak in the intensity for the in-plane rotationally distribution of the (110) planes is split into two, rotated by ±4.5° with respect to each other. The center, however, points into the ⟨10⟩ directions, which means that the Cu{110} planes are, except for the small rotation, parallel to Si{211} and not Si{110} as might be expected.
Acknowledgement

We would like to thank Lionel André for assistance with the synchrotron radiation measurements and the staff of the ESRF for providing the X-ray beam. A.R. gratefully acknowledges receipt of a stipend from the Fonds der Chemischen Industrie. This project has benefited from a collaboration contract under the Italian INFM/OGG with Roberto Felici. It was supported by the Deutsche Forschungsgemeinschaft (DFG) through SFB 569 and partly by the German BMBF under grant number 05KS1GUC/3.

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