Growth of Cu films on hydrogen terminated Si(100) and Si(111) surfaces

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We have employed reflection high energy electron diffraction (RHEED) and high resolution transmission electron microscopy (HREM) to study Cu films grown on hydrogen terminated Si(100) and Si(111) substrates by molecular beam epitaxy. X-ray diffraction and RHEED studies indicate ⟨100⟩Cu growth on Si(100) and ⟨111⟩Cu growth on Si(111). HREM reveals orientation relationships of $[001]_{Cu} \| [011]_{Si}$, $(010)_{Cu} \| (011)_{Si}$ and $[\bar{1}12]_{Cu} \| [011]_{Si}$, $(220)_{Cu} \| (11\bar{1})_{Si}$ for Si(100) and Si(111), respectively. A copper silicide layer forms on Si(100) with deposition and appears to aid in proper lattice matching. No significant interdiffused region was detected in the films deposited on Si(111), however, distinct orientational variants were observed in this case.

I. INTRODUCTION

Silicon is the most widely used substrate on which the growth of metals, semiconductors, and insulators has been studied. This is due to the availability of single crystal Si(100) and Si(111) wafers and the importance of silicon in semiconductor device technology. The growth of metal films on semiconductor surfaces continues to be an area of great research activity since the metal/semiconductor contact is not well understood.[1] The orientation relationship across such interfaces can significantly affect the electrical properties such as the density of interface states and Schottky barrier height.[2-4] In addition, interfacial electronic properties are very sensitive to small defect and impurity concentrations at the interface. Therefore, an awareness of the nature and quality of the metal/semiconductor interface is of considerable importance.

During the past few years, it has been shown that Si surfaces etched in hydrofluoric acid (HF) are hydrogen terminated.[5] Such surfaces are known to be inert for several minutes in air and for several hours in ultrahigh vacuum at room temperature.[6] This surface passivation is believed to be due to hydrogen termination of the dangling Si bonds, which renders the surface chemically stable.[5,7,8] Infrared spectroscopy studies have established the formation of silicon hydrides at the surface.[9,10] Scanning tunneling microscopy has shown that etching Si(100) and Si(111) with dilute HF (10%) solution produces surfaces with microscopic roughness (0.3 nm), whereas etching Si(111) with 40% NH_4F results in atomically smooth surfaces over areas on the order of 100 nm.[11] The creation of hydrogen terminated surfaces by chemical etching opens numerous possibilities for the epitaxial growth of various thin metal films. Such surfaces have already been employed to grow epitaxial Fe, Ag, and Au films.[12,13]

Ohmi *et al.*[14] reported epitaxial growth of (100) copper, deposited by rf-bias sputtering onto (100) Si. More recently, there have been reports of epitaxial growth of Cu on HF-etched Si(100) and Si(111) substrates under a base pressure of 10^{-7} Torr, using an ordinary e-beam evaporator.[15] Standard θ–2θ x-ray diffraction scans show only the Cu(200) peak for Cu growth on Si(100), with no trace of Cu(111), while only the Cu(111) peak appears for Cu grown on Si(111). Grazing angle x-ray diffraction measurements in the former case have shown an in-plane epitaxy of Cu(100) rotated 45° relative to the Si(100) lattice.[16] Epitaxial growth of Cu on a 7×7 reconstructed Si(111) surface at 100 °C has been reported as Si(111)‖ Cu(111) and Si[112]‖ Cu[110], resulting in a lattice mismatch of 15%.[17] Low energy electron diffraction (LEED) and high resolution transmission electron microscopy (HREM) results point to the presence of an interface alloy, possibly a metastable copper silicide, seemingly an important component in the growth of Cu(111) on Si(111). In this paper we examine the growth of Cu on hydrogen terminated Si(100) and Si(111) surfaces at room temperature under ultrahigh vacuum conditions. Reflection high energy electron diffraction (RHEED) was used to monitor the growth, quality, and structure of the films *in situ*. HREM was employed to examine interface and near-interface regions. Energy dispersive x-ray spectroscopy (EDXS) was performed to probe the compositional distribution of Si and Cu in the intermixed region. Differences in the growth of Cu on Si(111) and Si(100) are discussed.

II. EXPERIMENTAL

The films were grown in an ultrahigh vacuum using a molecular beam epitaxy (MBE) deposition system with a base pressure $<2\times10^{-10}$ Torr. Cu was evaporated using an electron beam evaporator with a computer-controlled pneumatic shutter. The growth chamber is equipped with a RHEED unit (15 keV). The sample can be rotated 360° with respect to the RHEED electron beam, allowing one to

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study the full azimuthal dependence of the RHEED pattern. The rate of deposition and total thickness were measured with quartz crystal thickness monitors calibrated using a diamond stylus profilometer. The deposition rates were 0.05–0.1 nm/s. During deposition the pressure was maintained at $<2\times10^{-9}$ Torr with the aid of a liquid nitrogen cryostatic shroud. A sample load-lock chamber connects a surface analysis chamber to the growth chamber. The surface analysis chamber is equipped with an Auger spectrometer, and a reverse view LEED unit.

Si(100) *p*-type and Si(111) *n*-type substrates (1 cm^2) were degreased and etched in a 10% HF-de-ionized water solution, pull dried, and loaded in to the load-lock chamber. After pumping for about 2 h the substrates were transferred in to the growth chamber. RHEED patterns taken from the Si substrates displayed sharp streaks and Kikuchi lines, indicating a clean and ordered surface. Some of the substrates were also analyzed by LEED which showed sharp spots. Auger spectroscopy on such a surface showed no trace of oxygen. Standard θ–2θ x-ray diffraction scans were performed on a Rigaku powder diffractometer, using Cu $K\alpha$ radiation.

Transmission electron microscopy (TEM) section samples were fabricated by bonding two films face-to-face, mechanical thinning, and ion beam milling. Analytical TEM was undertaken on a JEOL 2000FX, transmission electron microscope, operating at 200 kV, equipped with an x-ray energy dispersive spectrometer interfaced to a Noran Instruments 5502 microanalysis system. Atomic resolution TEM was performed on a JEOL 4000EX HREM operating at 400 kV, with point-to-point resolution better than 0.18 nm. For analysis, electron micrographs were digitized with a Cohu series 4810 solid state CCD camera into NIH image, version 1.35,[18] modified to incorporate a fast Hartley transform [fast Fourier transform (FFT)] routine.[19] Interplanar spacings of selected regions were determined with reference to a Fourier power spectrum taken from a silicon standard, viewed down a {011} direction.

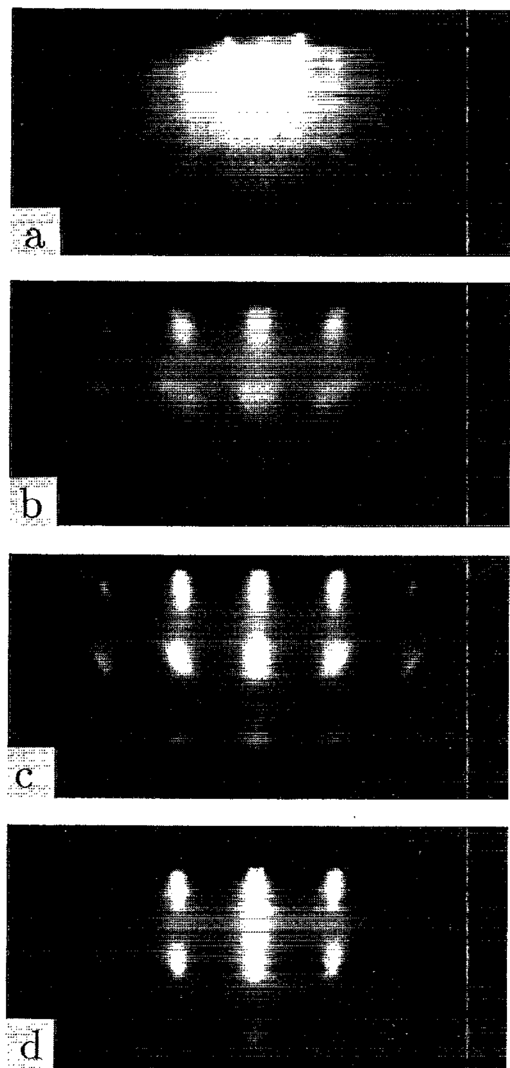

FIG. 1. (a) RHEED pattern obtained along Si⟨110⟩ azimuth on a clean Si(100) surface. Corresponding RHEED patterns after (b) 5 nm, (c) 25 nm, (d) 150 nm Cu deposition.

III. RESULTS AND DISCUSSION

A. Cu/Si(100)

We first discuss the RHEED results of the growth of Cu on Si(100) at room temperature. Figures 1(a)–1(d) show RHEED patterns for a clean Si(100) surface and for Cu depositions of 5, 25, and 150 nm, respectively, along the Si⟨110⟩ azimuth. Upon the initiation of Cu deposition, the sharp streaks of Si(100) are replaced by rather broad and diffuse spots. At a film thickness of about 10–15 nm, sharp elongated spots, characteristic of Cu appear, indicating that growth is epitaxial but three dimensional. Further deposition of Cu gives rise to somewhat sharper spot patterns. The Cu RHEED patterns confirm the full azimuthal symmetry of the two-dimensional Cu(100) lattice and its rotation of 45° with respect to Si(100). X-ray diffraction (θ–2θ) scans on a 150 nm thick Cu layer show only Cu(200) peaks, in agreement with Chang.[15] The substrate temperature prior to Cu deposition was observed to affect growth quite significantly. When the substrate was cooled to 0 °C, the deposition of Cu resulted in a ring diffraction pattern, indicating that the Cu film was polycrystalline. At higher substrate temperatures (e.g., 50–100 °C), the RHEED patterns for Cu again took the form of broad and diffuse spots which did not change appreciably, even after 100 nm of Cu deposition.

In the following we discuss the TEM results of a sample grown at room temperature. Figure 2 depicts the Cu/Si(100) interface, viewed along the Cu [Fig. 2(a)] and Si [Fig. 2(b)] phase boundaries. Clearly, interdiffusion has taken place during growth. The interdiffused region (upper portions of Fig. 2) was found to be on the order of 10 nm in extent. Examination of the Fourier power spectra (Fig. 2 insets) from the Cu and Si regions [bottom-half of Figs. 2(a) and 2(b)] reveals an orientation relationship of $[001]_{Cu} \| [011]_{Si}$ and $(010)_{Cu} \| (011)_{Si}$. This corresponds to a relative rotation of 45° between the lattices. This 45° rotation agrees well with results previously cited by Chang *et al.*[16] for electron beam evaporated Cu films on ⟨100⟩Si

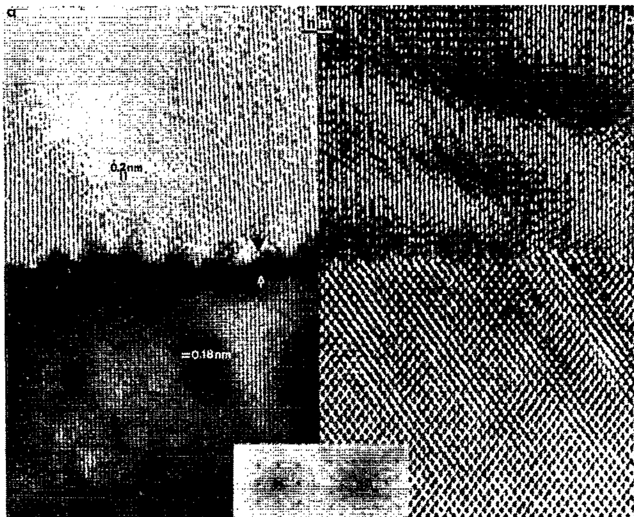

FIG. 2. Atomic resolution micrograph from a Cu/Si(100) sample taken along Si⟨011⟩, showing the Cu–Si interdiffused layer bordering (a) Cu⟨001⟩, (b) Si⟨011⟩. Arrows in (a) illustrate atomic plane bending across the interface. Insets show corresponding FFT power spectra.

and with our RHEED results above. Measurements of FFT patterns from the Cu region yield an interplanar spacing of 0.18 nm, corresponding to the {002} Cu reflections (the {022} planes are just below the instrument resolution limit).

Energy dispersive x-ray spectroscopy was performed using a nominal 10 nm diam probe. Figures 3(a)–3(c) show the resulting spectra, obtained from the Cu region [Fig. 3(a)], the interdiffused region [Fig. 3(b)], and the Si substrate [Fig. 3(c)]. The interdiffused region [Fig. 3(b)] is clearly shown to be a Si–Cu mixture [the small Si peak in Fig. 3(a) is a detector artefact, and is present at the same level in all the spectra]. Analysis of FFT patterns from the interdiffused region reveals the interplanar spacing to be 0.2 nm. From the Cu–Si binary phase diagram,[20] Cu_3Si is the most stable phase at room temperature. The above interplanar spacing most nearly corresponds to either the (320) or the (312) planes of Cu_3Si. Sasnowski *et al.*[21] have reported Si–Cu interdiffusion in 100 nm thick Cu films (from x-ray photoelectron spectroscopy studies), deposited on Si(100). However, in that work, strong epitaxial growth was not observed. Chang *et al.*[15] cite diffraction peaks corresponding to Cu_3Si in electron-beam deposited Cu films on Si(100).

We also wish to point out the strong strain contrast observed at the Cu/Cu–Si interdiffused region interface. Close examination of this interface reveals a bending of atomic planes in crossing the boundary [indicated by arrows in Fig. 2(a)]. This is reasonable in light of the interplanar spacing discrepancy [~10% mismatch between Cu(002) and Cu–Si] along this interface.[22] The Si/interdiffused region interface [Fig. 2(b)], however, displays little or no strain contrast, since the lattice mismatch is only ~3% in this case [Cu–Si and Si(220)]. The Si(111) planes form an even better match in projection along the interface. Close inspection of Fig. 2(b) shows that the

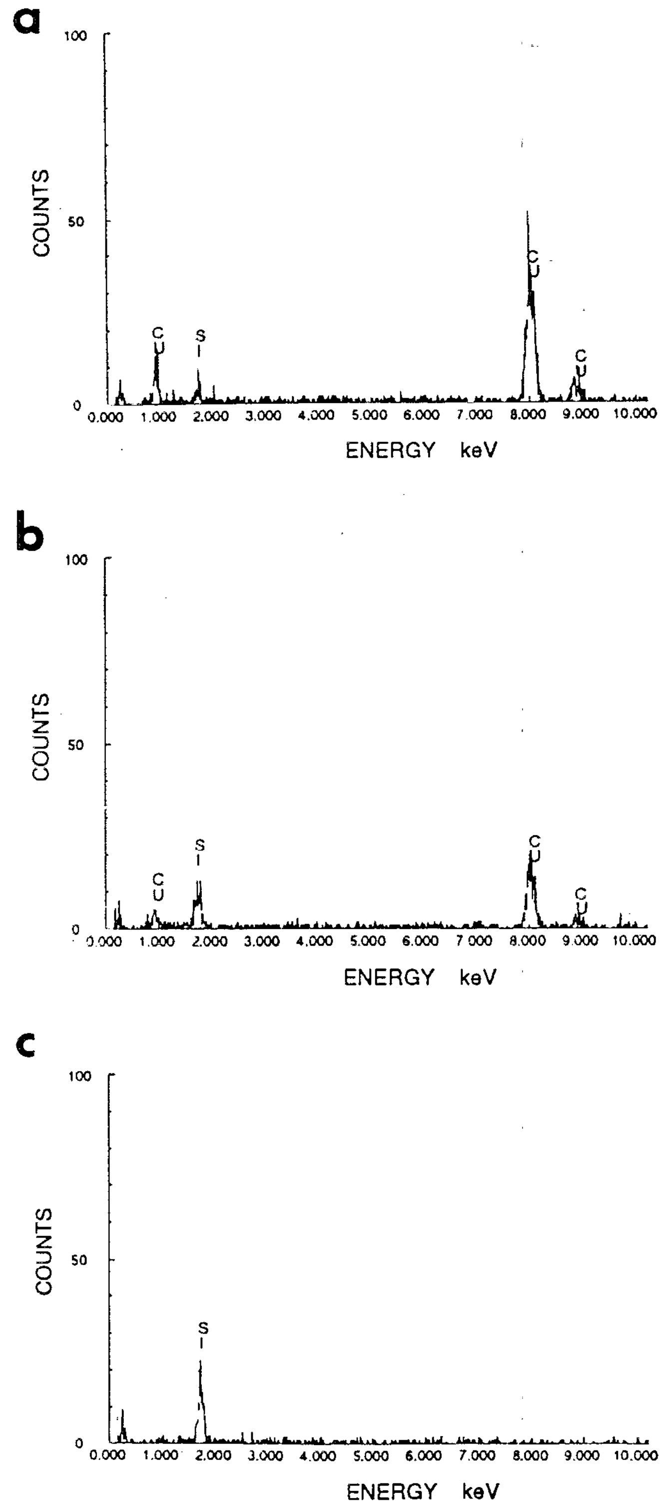

FIG. 3. Energy dispersive x-ray spectra from (a) Cu, (b) Cu–Si interdiffused region, (c) Si substrate. The small Si peak in (a) is a detector artefact.

Si(111) and copper silicide planes meet at ~55° angle. In projection along the interface, the Si(111) planes are spaced 0.39 nm apart, while twice the silicide spacing is 0.4 nm, giving rise to a mismatch on the order of 2.5% along

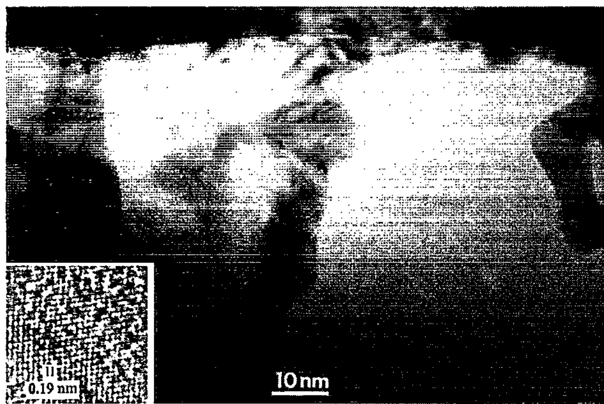

FIG. 4. TEM micrograph of the Cu/Si interface, displaying interdiffused spikes. The inset is an atomic resolution micrograph from one such region.

the interface. Figure 4 reveals the presence of interdiffused "spikes," extending into the silicon substrate. Analysis of FFT power spectra in one such region (inset to Fig. 4) results in interplanar spacings of 0.28 and 0.19 nm.

We should also note that the observation of this 10 nm thick interdiffused region is consistent with the *in situ* RHEED studies on the growing film, cited above, in which the patterns are initially diffuse during growth of the first 10 nm of film, before reverting to a more three-dimensional single crystal spot pattern, characteristic of Cu.

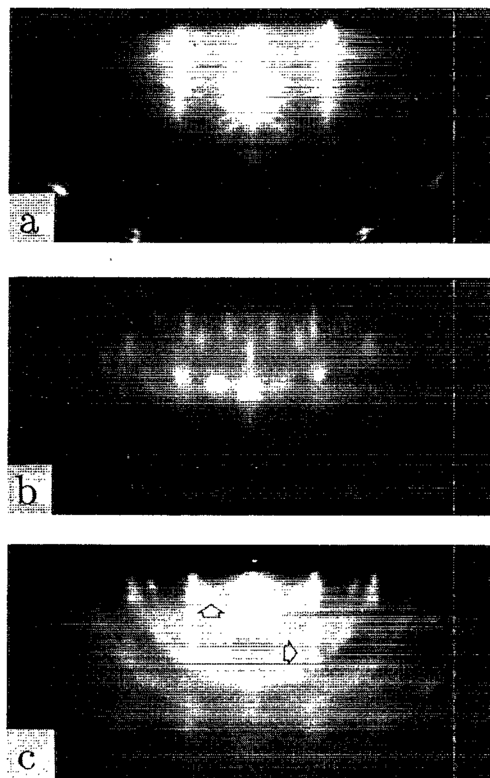

FIG. 5. (a) RHEED pattern obtained along Si⟨211⟩ azimuth on a clean Si(111) surface. Corresponding RHEED patterns after (b) 5 nm, (c) 150 nm Cu deposition.

B. Cu/Si(111)

RHEED observations of the growth of Cu on Si(111) at room temperature did not reveal completely epitaxial growth. Upon initial Cu deposition, the Si(111) diffraction streaks corresponding to the substrate disappeared with a concomitant increase in the background intensity. An increase in Cu thickness to approximately 1 nm resulted in a faint spot pattern with sixfold symmetry, indicating three-dimensional growth. Figures 5(a) and 5(b) show the RHEED patterns along Si⟨211⟩ azimuth of a clean Si(111) surface before and after depositing 5 nm of Cu. With increasing thickness, the spot pattern persisted superposed on faint diffraction rings as shown in Fig. 5(c) for a 150 nm thick Cu film. However, no distinctive patterns were observed along the Si⟨110⟩ azimuth. Measurements taken from the most intense reflections in Fig. 5(c) corresponded to interplanar spacings of lattice planes along Cu⟨110⟩ and Cu⟨111⟩. Both of these values were obtained using the silicon substrate pattern as a calibration standard, taking into account the geometry of experimental configuration. This observation indicates that the Cu lattice is rotated by 30° with respect to the Si lattice, as corroborated by the TEM results below. Out-of-plane θ–2θ x-ray diffraction scans on such films showed only the Cu(111) peak, which is consistent with the RHEED patterns described above. Other faint spots observed [indicated by arrows in Fig. 5(c)] are believed to be related to the presence of discrete orientational variants within the film, which were revealed in TEM images. Varying the substrate temperature (<100 °C) did not produce noticeable changes in the RHEED data.

Next we describe our TEM results. Figure 6 shows a Cu/Si(111) interface, imaged at atomic resolution. In contrast to the Cu/Si(100) case, little or no interdiffused regions are noted. This is verified by the continuity of atomic planes extending to the interface. Examination of both atomic structure images and the corresponding FFT power spectra (insets to Fig. 6) reveal the orientation relationship to be $[\bar{1}12]_{Cu} \| [011]_{Si}$ and $(220)_{Cu} \| (11\bar{1})_{Si}$. Analysis of FFT power spectra from copper regions yield interplanar spacings of 0.19 and 0.25 nm for the (111) and (044) planes, respectively. At first sight, there would appear to be little matching with the 0.313 nm Si(111) planes. However, close examination of Fig. 6 reveals that the (220)Cu and the (111)Si planes meet nearly parallel to one another across the interface. The relatively large ($\sim 20\%$) mismatch is accommodated by numerous misfit dislocations (indicated by arrows in Fig. 6). Incorporation of these dislocations largely relieves the strain at the interface, as evidenced by the lack of substantial strain contrast at the interface [compare to Fig. 2(a)]. An interesting feature of this film is the presence of discrete orientational variants or domains (lower center inset to Fig. 7). FFT spectra from individual domains (upper-left-hand and lower-right-hand insets to Fig. 7) reveal misorientations on the order of 70° between (111) planes within each domain. It is well

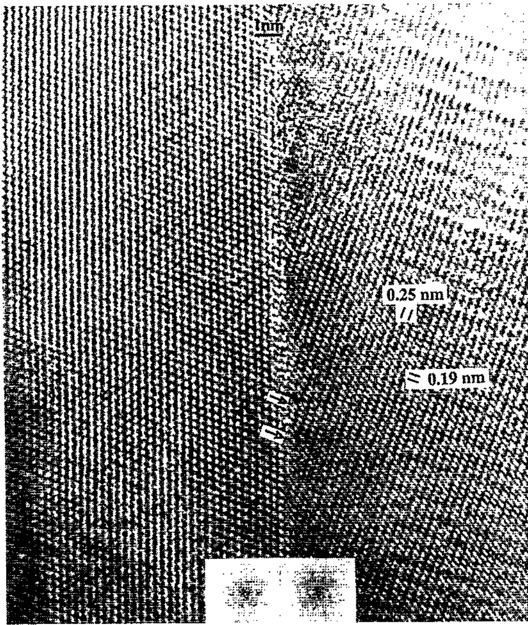

FIG. 6. Atomic resolution micrograph from a Cu/Si(111) sample taken along Si⟨011⟩, showing the Cu⟨112⟩/Si⟨011⟩ interface. Arrows indicate some of the numerous misfit dislocation present along the boundary. The insets show corresponding FFT power spectra.

known[23] that face centered cubic metals readily form twins on {111} planes. Along ⟨112⟩ (Fig. 7), a {111} twin plane, separating two such domains, is viewed edge on. Bai *et al.*[24] have detected twin-related (111) planes in azimuthal x-ray scans of Cu film deposited by a partially ionized beam onto Si(111). These results are also consistent with the *in situ* RHEED results above, in which the patterns from the growing Cu film are diffuse and include extra spots.

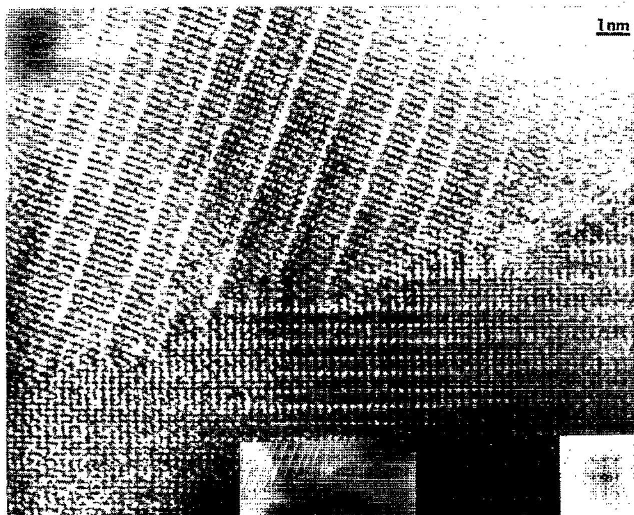

FIG. 7. Atomic resolution micrograph from a Cu/Si(111) sample taken along Si⟨011⟩, showing the boundary between two Cu⟨112⟩ orientational variants. The lower inset is a lower magnification view. Upper-right-hand and lower-left-hand insets show corresponding FFT power spectra.

We also note that no interdiffused spike regions were noted in these films. Chang[15] has found an orientation dependence for the Cu–Si reaction, which strongly favors silicide formation on (100) surfaces in preference to (111) surfaces. In that work, it was argued from broken Cu–Cu and Si–Si bond considerations in both the fcc Cu and diamond cubic Si lattices that overall, silicide formation is energetically favorable on the (100) surface. This is consistent with the results found in this work.

The epitaxial growth of Cu on 7×7 reconstructed Si(111) surface at room temperature has been reported using the partially ionized beam method.[24] A mechanism of epitaxial growth of Cu(111) on Si(111) substrate was proposed via an η''-Cu_3Si intermediate phase. Walker *et al.*[16] have obtained LEED, RHEED, and subtle HREM evidence for copper silicide formation at the interface of MBE grown copper films on Si(111). Upon close examination of Fig. 6, one can identify regions where such a silicide may be present. However, any alloying is insignificant in comparison to the Si(100) case above and is not thought to play a major role in promoting epitaxial growth.

IV. SUMMARY

Our RHEED and TEM observations on Cu films grown on hydrogen terminated Si(111) substrates indicate the presence of epitaxial Cu crystallites with discrete orientational variants but not completely epitaxial films. On the other hand our studies confirm epitaxial growth of Cu(100) on hydrogen terminated Si(100) substrates. An interfacial Cu silicide region seems to aid the epitaxial growth of Cu on Si(100) by providing a lattice match. Such an intermixed region was not detected in the case of Cu grown on Si(111), which may account for the lack of long range epitaxy.

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