

Epitaxial growth of Cu (001) on Si (001): Mechanisms of orientation development and defect morphology

I. Hashim, B. Park,^{a)} and H. A. Atwater

Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125

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We describe the evolution of microstructure during ultrahigh vacuum ion beam sputter deposition of Cu (001) at room temperature on hydrogen-terminated Si (001). *In situ* reflection high energy electron diffraction indicates growth of an epitaxial Cu (001) film on Si (001) with the intensity of the Bragg rods sharpening during 5–20 nm of Cu film growth. Post-growth x-ray diffraction indicates the Cu film has a mosaic spread of (001) textures of about $\pm 2^\circ$ and that a small fraction (0.001–0.01) is of (111) textures. High-resolution transmission electron microscopy shows an abrupt Cu/Si interface with no interfacial silicide, and reveals an evolution in texture with Cu thickness so as to reduce the mosaic spread about (001). Moiré contrast suggests a nearly periodic elastic strain field extending into the Cu and Si at the interface. Other aspects of film growth which are critical to epitaxy are also discussed.

The growth of single-crystal copper films on silicon is potentially of great technological interest both as a convenient template for the preparation of other metallic films in magnetic thin film applications, and as an interconnect material for future large-scale integrated circuits.¹ Recently, considerable controversy has surrounded reports of growth of epitaxial Cu films on Si. Successful epitaxy of Cu (001) on Si (001) was reported for growth in vacuum systems with base pressures in the high-vacuum range,^{2,3} but the analysis of microstructure was limited to x-ray diffraction in conventional θ - 2θ geometry and ion channeling. On the other hand, surface science investigations employing photoelectron holography⁴ indicated the absence of (001) epitaxial growth on Si (001) 2×1 structures under ultrahigh vacuum conditions.⁴ Furthermore, there have been conflicting reports of silicide formation upon deposition of Cu on Si at low temperatures (0–100 °C). Walker *et al.*^{5,6} reported η -Cu₃Si formation upon deposition at 100 °C of Cu on Si(111) which aided the establishment of an epitaxial relationship between Cu and Si. Ichinokawa *et al.*⁷ observed an intermixed layer of Cu and Si at room temperature deposition on Si(001) 2×1 surface. Also, Sosnowski *et al.*,⁸ who used ionized cluster beam deposition at room temperatures, did not find any evidence for an interfacial reaction between Cu and Si. Phase formation in Cu-Si diffusion couples in the temperature range 200–260 °C was investigated by Hong *et al.*⁹ Harper *et al.*¹⁰ reported an epitaxial relationship between Cu₃Si and Si(001) which was formed upon deposition of Cu on Si(001) at 200 °C by dc magnetron sputtering. This silicide phase catalyzed a remarkably rapid oxidation of Si at room temperature, leading to the formation of over 1- μ m-thick buried SiO₂/Si(001). The purpose of this letter is to resolve some of these controversies, and to show how orientation and microstructure develop during epitaxial growth of Cu on Si (001).

Films were grown in a custom-designed, load lock-equipped ultrahigh vacuum ion beam sputtering system with base pressure in the mid- 10^{-10} Torr regime. Prior to sample insertion into the vacuum system, samples were cleaned by sequential chemical oxidation in a 5:1:1 solution of H₂O:HCl:H₂O₂ at 80 °C, followed by etching in a buffered HF solution. Upon insertion into the sputtering system chamber, reflection high energy electron diffraction (RHEED) at 15 keV was used to confirm (1 \times 1) surface reconstruction of the (001) Si that is commonly observed on HF-dipped Si (001), and which corresponds to dihydride termination of the surface.¹¹ The as-inserted Si (001) substrates were heated to $T=200$ °C for approximately 2 h and cooled to room temperature at a cooling rate of 3 °C/min, prior to sputter deposition of Cu.

Cu was deposited onto dihydride-terminated Si surfaces by ion beam sputtering at a deposition rate of approximately 0.10 nm/s. The film thickness, estimated during growth using an oscillating-crystal thickness monitor, was confirmed afterwards with Rutherford backscattering spectrometry. The purity of the Cu film was confirmed using electron microprobe analysis which indicated less than 0.2 at. % Ar. *In situ* RHEED measurements indicated that the [100] and [110] in-plane azimuths were parallel to [110] and [100] azimuths of Si, respectively, and are shown as insets to Figs. 1(a) and 1(b). The lattice mismatch for the orientation Cu[100]|| Si[110] is 6% as opposed to 33% when the two unit cells are parallel. Information about the evolution of the film microstructure during growth was also obtained using *in situ* RHEED measurements which were recorded on video and later analyzed to calculate the intensity profile across the Bragg rods. As indicated by RHEED measurements shown in Fig. 2, during growth of the first 2 nm of copper, broad and diffuse Bragg rods corresponding to a nominally (001)-textured Cu film were observed. For thicknesses in the range 5–10 nm, the Bragg rod width gradually decreased whereas its intensity gradually increased with increasing Cu thickness. No significant changes in the RHEED features were observed for thicknesses greater than 20 nm. The change in the relative intensities of the 01 and 0 $\bar{1}$ peaks in Fig. 2 for thicknesses

^{a)}Present address: School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245.

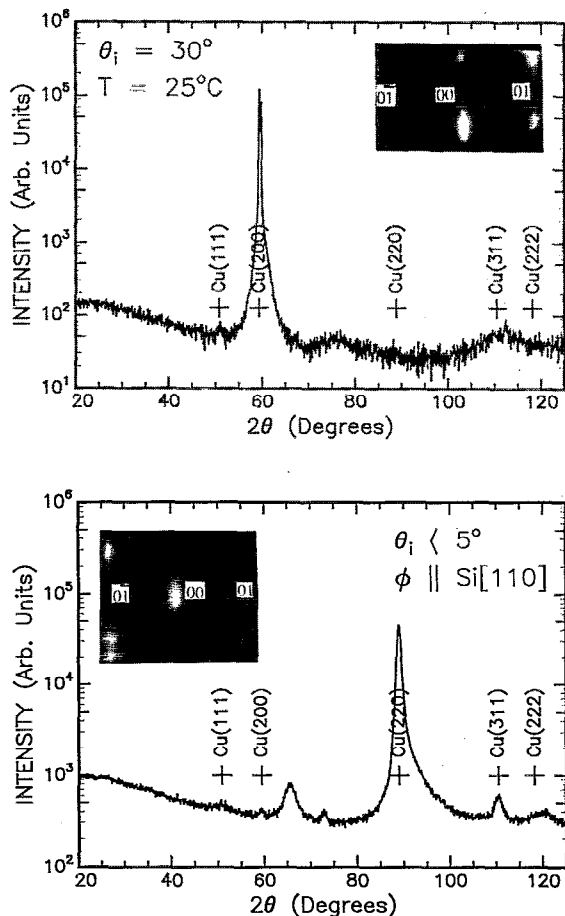


FIG. 1. X-ray diffraction scans of epitaxial Cu(001) film on Si(001) deposited at room temperature, for (a) $\theta_i = 30^\circ$ and (b) $\theta_i = 5^\circ$ along [110] Si azimuth. The insets show the RHEED patterns during film growth observed for [100] and [110] Cu azimuths, respectively.

greater than 5 nm is due to variations in the sample alignment with respect to the electron beam during growth.

Crystallographic texture of the Cu films on Si was assessed by x-ray diffraction. Measurements were performed using a Co- K_α x-ray source with fixed incident beam angles in the range from 5° to 45° in 5° intervals, along both the [100] and [110] azimuths of the Si surface. Scattered x-rays were measured using a parallel detection and data acquisition instrument simultaneously over an angular range of 120° with 0.05° angular resolution. While not a complete pole figure analysis, these measurements do probe a wide range of reciprocal space, and provide a more comprehensive indication of film texture than can be obtained from a single θ - 2θ diffraction measurement.^{2,3}

Figure 1(a) shows the x-ray diffraction spectrum for $\theta_i = 30^\circ$ which is equivalent to the more conventional θ - 2θ x-ray scattering geometry. For Co- K_α , 2θ for Cu(200) reflection is close to 60° . Therefore, this reflection should be much stronger than other reflections of fcc Cu, which is indeed the case, as shown in Fig. 1(a) for $\theta_i = 30^\circ$. Other textures of fcc Cu, notably (111), are detectable through their intensity are 2–3 orders of magnitude smaller than (200). Figure 1(b) illustrates a diffraction spectrum for grazing angle incident beam ($\theta_i < 50^\circ$) along the [110]Si

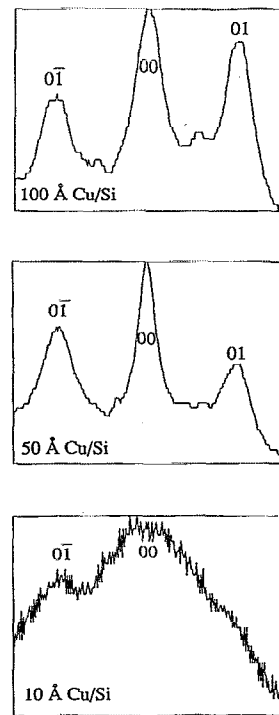


FIG. 2. The intensity profile across RHEED patterns at various stages of Cu(001) film growth on Si(001).

zone axis. In this geometry, the x-ray scattering vector is close to being in the plane of the sample, and hence, sensitive to the in-plane orientation of the film texture. For near-zero incident angle and Cu[100] azimuth, a strong Cu(220) reflection should be observed from an epitaxial Cu(001) film. As shown in Fig. 1(b), a strong Cu(220) reflection is indeed observed for this azimuth whereas for Si[100] azimuth, the reflection completely disappears, thus confirming the orientation Cu[100]|| Si[110]. No reflections corresponding to copper silicide phases were detected for films deposited at room temperature. Room-temperature-deposited Cu(001) films with very strong texture (i.e., competing texture fraction < 0.005) exhibited no silicide formation even after annealing at 120°C for 2 h. On the other hand, a silicide was formed immediately upon deposition at 80°C . This was evidenced by the absence of a Cu(001) RHEED pattern, the film being unlike in appearance to that of Cu, and identification of Cu_3Si peaks in its x-ray diffraction spectrum. This suggests the possibility of a kinetic barrier for silicide nucleation in well-oriented Cu(001)-Si(001) bilayers and that this barrier is either absent or smaller during the initial stages of film growth. It is possible for other metastable silicide phases to be present during interfacial reaction of Cu and Si as observed by Hong *et al.*⁹ For certain Cu films where trace metallic impurities such as Fe, Cr, and Ni were detected by electron microprobe analysis, in amounts 0.1%–1%, polycrystalline films with strong (111) texture were obtained, as indicated by x-ray diffraction analysis.¹² Cross-sectional transmission electron microscopy (XTEM) studies of these films revealed an interfacial

silicide less than 1-nm thick separating the columnar grains of (111)-oriented Cu film and Si substrate.¹² It is plausible that the presence of impurities such as Fe and Cr catalyzed an interfacial silicide formation upon deposition of Cu, thus promoting (111)-textured polycrystalline growth. Furthermore, in another experiment a 50-nm-thick Cu film was heated to 230 °C until it was completely consumed to form Cu₃Si, based on reaction kinetics reported by Hong *et al.*⁹ This was followed by deposition of another 50 nm of Cu film at room temperature. The film subsequently deposited was found to be polycrystalline with strong (111) texture.

Transmission electron microscopy (TEM) was done using a Philips EM430 microscope operating at 300 keV, and sample preparation was done using adhesives which did not require any high-temperature curing. The samples were ion milled using Ar⁺ at 77 K, 10 min prior to insertion into the microscope. A high-resolution cross-sectional transmission electron micrograph of the Cu/Si interface along the [110] zone axis of Si, for a room-temperature-deposited sample, is shown in Fig. 3(a). The inset shows the [110] and [100] selected area diffraction pattern due to Si and Cu, respectively. The spots due to Cu are broader than those due to Si and have a mosaic spread of $\pm 2^\circ$ about Si [110] zone axis. Furthermore, the interface is atomically sharp with no evidence of any interfacial silicide. Interestingly, Fig. 3(a) illustrates that grains with orientations other than (001) can be observed within the first 5 nm of Cu film, which is in agreement with x-ray analysis and RHEED observations. These grains are occluded during the early stages of Cu growth by grains of (001) orientation, eventually leading to a single-crystal Cu(001) film after about 20 nm. This evolution of microstructure by occlusion is summarized in a schematic diagram [Fig. 3(b)] showing the distribution of orientations as obtained from cross-sectional transmission electron micrograph shown in Fig. 3(a).

A nearly periodic strain field can be observed extending into the first 2–3 nm of Cu film as well as the Si substrate, as can be seen in lower magnification cross-sectional electron micrographs.¹³ The period of this strain field (\approx nm) agrees well with the periodicity corresponding to the 6% mismatch between Cu and Si for Cu[100]|| Si[110]. It is possible that each strained region near the interface corresponds to a growing Cu island at the early stages of growth and these islands coalesced to form a columnar-grained film. Bright-field XTEM analysis indicated a high density of dislocations present in the film, as well as a polycrystalline copper oxide up to 20-nm thick at the Cu film surface. The grains due to the copper oxide give the Cu film the appearance of a polycrystalline film in plan view TEM.¹³

In conclusion, we have defined conditions for which Cu(001) epitaxy is possible on H-terminated Si(001), in ultrahigh vacuum conditions. The RHEED, x-ray diffraction, and electron microscopy results suggest that the mechanism for orientation development is an occlusion of grains misoriented with respect to (001) grains eventually

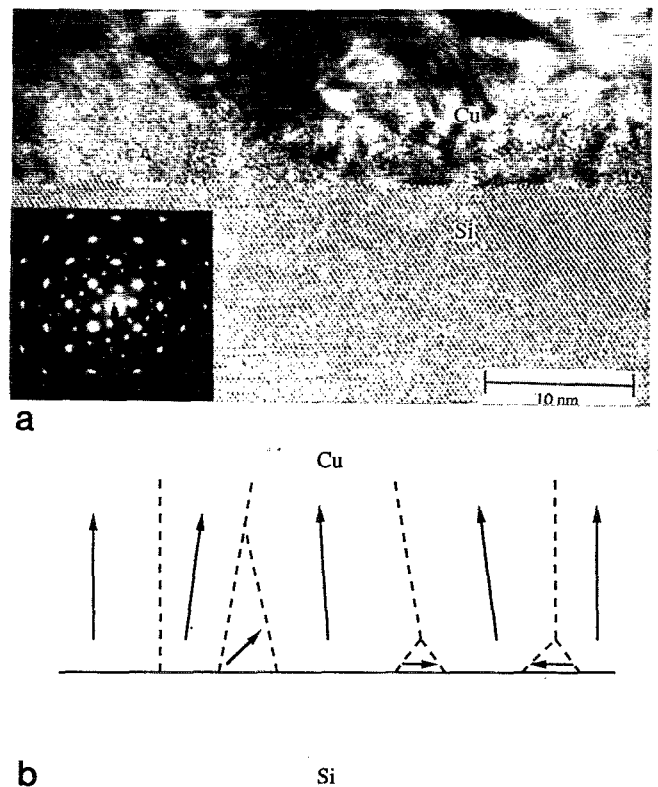


FIG. 3. (a) High-resolution XTEM, along [110] Si zone axis, of Cu film on Si. The Si [110] and Cu [100] selected area diffraction pattern is shown as inset. (b) Schematic showing microstructure evolution as obtained from high-resolution XTEM image.

leading to a reduction in the mosaic spread of the columnar-grained structure. No evidence suggesting an interfacial silicide was found for room temperature (001) Cu film growth. However, for (111)-textured polycrystalline Cu films, an interfacial silicide was observed which inhibited Cu(001) epitaxy on Si(001).

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