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Critical height and growth mode in epitaxial copper nanowire arrays fabricated using glancing angle deposition

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The growth and resulting crystallography of Cu nanowire arrays fabricated using glancing angle deposition are studied. On native oxide Si(100), the nanowires exhibited a strong (110) texture for a deposition angle $\theta=75°$ with rotational symmetry of the low energy Cu[111] about the long axis. On hydrogen-terminated Si(110), the wires are epitaxial with the substrate. The critical height for epitaxial growth is maximal at $\theta=35°$, and decreases rapidly with increasing deposition angle. Based on the growth mechanisms in glancing-angle-deposited materials, the theory of growth mode in epitaxial thin films, and the observations about texture formation in epitaxial and nonepitaxial Cu nanowires; we discuss the observed growth modes in epitaxial nanowire arrays. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1891287]

Glancing angle deposition with substrate rotation (GLAD) has been developed[1] to fabricate porous nanostructures in three dimensions. The morphology can be controlled by the deposition parameters such as the deposition angle, rotation rate, deposition rate, background gas pressure, temperature; and material specific properties such as melting point, chemical bonding and surface diffusion constant. Due to the special microscopic wirelike morphology, obliquely deposited films possess unique magnetic, electrical, optical, mechanical, thermal transport, and crystalline anisotropic properties.[2–7] GLAD films are already used for technological applications[8,9] and are considered to be promising candidates in many other fields.[6,10]

Figure 1 shows tapping mode atomic force microscopy images of Cu deposited on H-terminated Si(110) substrates at different incidence angles with a constant azimuthal rotation rate of 0.01 rot/s. The thickness was monitored by a quartz crystal microbalance placed near the substrate at normal angle to the flux. The effective film thickness was calculated taking into account the sample inclination angle relative to the flux central direction. The deposition rate was about 3 Å/s and the chamber pressure was in the upper 10^{-7} Torr range. During the growth of GLAD films, the incident flux of materials that come to the surface is preferentially deposited onto the top of the highest features, which cast a shadow on the neighboring surfaces. Hence, morphology and growth dynamics are mainly determined by the competition between self-shadowing and surface diffusion.[11]

While so much work has been devoted to understand and control the effect of the deposition parameters on the morphology and the microscopic structure,[11,12] there has been less of an attempt to understand the growth mode and mechanisms that lead to the texture formation in GLAD nanowires. In contrast to the crystallographic growth in continuous films, GLAD nanowires grow in all three dimensions on a nanometer scale. Consequently, the surface energies of the film stand in a different relationship to the bulk energies.

Recently,[13] we proposed a method to determine the texture orientation in GLAD nanowires using x-ray diffraction. In addition to the standard $\Theta-2\Theta$ scan, which yields the out-of-plane texture, in-plane scans of the Φ angle and, more importantly, polar scans of the Ψ angle are necessary to determine the distribution of selected crystallographic directions relative to the wire long axis. In the case of fcc Cu, the most relevant orientation is Cu(111) which corresponds to the close packed low-energy plane. Depending on the substrate surface symmetry and deposition parameters, the Cu(111) direction may not be collinear with the wire growth direction. In this case, the low-energy crystallographic direction will have rotational symmetry due to the azimuthal rotation of the substrate during the deposition. For instance, we have shown[13] that the low-energy orientation for fcc Cu deposited on native oxide Si(100) substrate at $\theta=75°$ has a conelike azimuthal distribution about the wire long axis, with the Cu[110] pointing normal to the substrate. Another example is bcc tungsten deposited on native oxide Si(100) at $\theta=87°$.[14] For W, the same structural distribution with the low energy orientation, bcc W(110), having rotational symmetry about the wire long axis. The latter has W(100) texture.

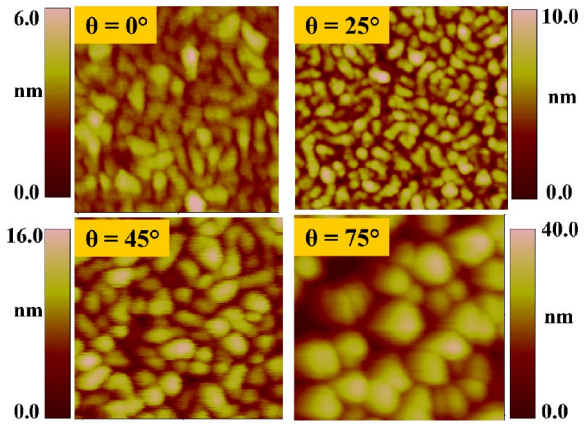

FIG. 1. Amplitude force microscopy images (500×500 nm) of epitaxial Cu films grown on H–Si(110) at different incident angles. As the angle of incidence increases, the wires grow as isolated columns with increasing height, diameter, and interspacing.

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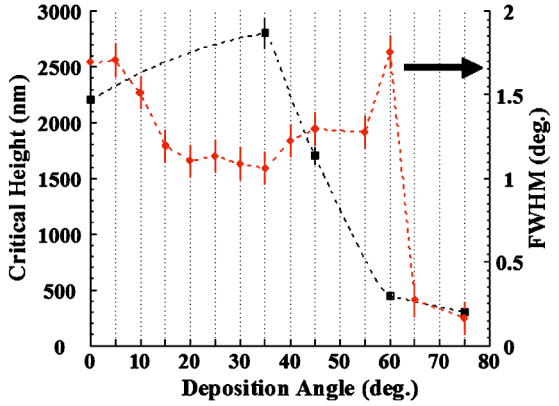

FIG. 2. Epitaxy critical height, and full width at half maximum (FWHM) of 300-nm Cu[111]/H-Si(110) films as a function of the deposition angle. Up to the deposition angle 60°, the critical height is consistent with the epitaxial growth quality. The strong reduction in the FWHM at higher angles is due to the split in the rocking curves.

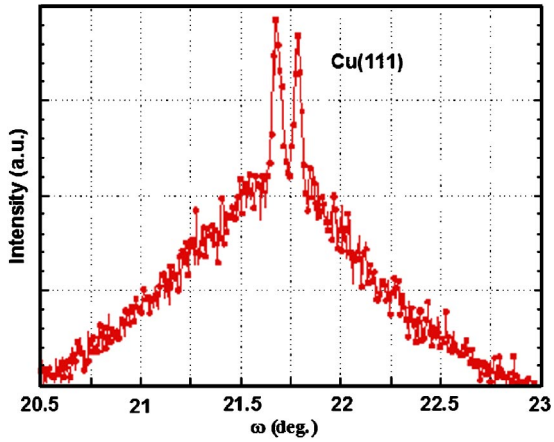

FIG. 3. Rocking curve of the Cu[111] crystallographic orientation of 300-nm epitaxial nanowire arrays deposited on H–Si(110) at 75°. The split in the rocking curve is due to the effect of the parallel momentum of incident adatoms on the Cu[111] crystallographic orientation.

In order to further investigate the mechanisms behind the texture formation in GLAD nanowires, we chose an epitaxial system that favors Cu(111) texture formation along the wire long axis.[15] On H–Si(110) substrates, the wires maintain an epitaxial relationship to the substrate [Cu(111)//Si(110)]. Figure 2 shows that the critical height,[16] where the epitaxial relationship breaks down, is dependent on the deposition angle. The critical height was determined using the appropriate x-ray diffraction technique.[15] We define the critical height as the film thickness where additional texture peaks begin to occur. This is determined within 50 nm using a series of films with different thickness. The height is maximal at a deposition angle of about 35°, which is consistent with the locally higher degree of crystallographic orientation, compared to the full width at half maximum (FWHM) of films deposited at lower angles. As the deposition angle is increased, the FWHM increases, and the critical height decreases to about 300 nm at $\theta=75°$. At large angles ($\theta \geqslant 65°$), the rocking curves of the Cu[111] crystallographic orientations show split diffraction curves with significantly sharp peaks (Fig. 3) and a strongly reduced FWHM (Fig. 2), indicating that there are distinct high quality orientations with rotational symmetry.

At large incidence angles, the diffusion is considerably larger and takes place preferably in the direction defined by the projection of the vapor beam direction onto the film surface. It has been verified[17] that the amount of kinetic energy preserved in the direction parallel to the film surface is determined by the angle of incidence, which explains the gradual decrease in the degree of orientation at intermediate angles. By contrast, at small angles ($\theta \leqslant 40°$), the effect of the parallel momentum is small compared to the isotropic surface diffusion of Cu adatoms.

Growth mode in epitaxial GLAD films: While the growth mechanism of epitaxial films deposited at polar angles smaller than 40° is to a vast extent identical to films grown at normal incidence, the shadowing length and the unidirectional diffusion have a strong impact on the texture formation in GLAD nanowires deposited at larger angles. We have identified two distinct behaviors corresponding to intermediate and large deposition angles.

Large deposition angles correspond to $\theta \geqslant 65°$. At the submonolayer level, the initial flux of material that arrives at the surface at an oblique angle is preferentially deposited on top of higher surface features, where the atoms occupy well-defined adsorption sites imposed by the regularity at the substrate surface.[18] This selective growth mode leads to the nucleation of solid clusters from the vapor phase that condense as three-dimensional islands on the substrate.[19] This behavior is conforming to the Volmer–Weber growth mode.[20] Within each island, short-range adatom–adatom interactions favor the interparticle separation of the adsorbate, while the adatom–substrate interactions favor an interparticle separation commensurate with the substrate lattice constant. In the case of Cu/Si(110) epitaxy where the lattice misfit (5.7%) is well below 10%,[21] the Cu epilayer strains uniformly to match its lattice constant to that of the Si-substrate. The uniformly strained islands constitute the template for subsequent growth of the epitaxial nanowire arrays.

Due to the identical chemical properties, the growth proceeds layer-by-layer within each island, conforming to the Frank–van der Merwe growth mode.[20] The succeeding overlayers will easily accommodate the lattice constant in coherence with the underlying layer, and thus also be in state of uniform strain. As the thickness increases, the epitaxial nanoarrays accumulate elastic energy with each additional layer up to the critical nanowire height. At this stage, the structural stability is lost and misfit dislocations occur at the interface to relieve the misfit strain. Since the strain energy is a function of the volume of layers,[21] one expects that the critical height in the isolated GLAD Cu nanowires will be much larger than in a continuous Cu film deposited at normal incidence (2200 nm), if the kinetics of adatoms were the same in both processes. In fact, the unidirectional diffusion arising from the incident adatom parallel momentum effect[22] has been identified to be responsible for the reduction in the thickness limit of epitaxial Cu-nanowire arrays.

With increasing thickness, the stress applied on the Cu lattice diminishes and the impinging adatoms are no longer totally incorporated in the Cu lattice, causing misfit dislocations at a much-reduced critical height. At this stage the recrystallization process is started. Nanowires with higher aspect ratio show additional texture peaks with rapidly increasing preference for the Cu(311) plane to be parallel to the underlying Cu(111) plane,[15] due to the low lattice misfit, and azimuthal distribution of the Cu(111) direction about the

wire's long axis. At this final stage, oriented crystallites will grow according to the evolutionary selection principle,[23] which takes place because of the differences in the growth rates of different crystal planes.

For intermediate deposition angles, the angle of incidence ranges between 45° and 60°. At the submonolayer level the Stranski–Krastanov growth mode[20] is more likely to take place since the islands will coalesce to form a continuous film due to the shorter shadowing length and high surface diffusion. As the layer thickens, the film roughens up and the growth proceeds stronger in the vertical direction[24] up to the critical height. Since the momentum effect is a function of the deposition angle,[17] the critical height in this domain is larger than in the large angle domain (Fig. 2).

In this work we studied the texture formation mechanisms in epitaxial and nonepitaxial GLAD Cu-nanowires as well as the dependence of the critical height on the deposition angle. Based on these observations, the interplay between the shadowing and diffusion mechanisms, and the theory of structural transitions in epitaxial overlayers of thin films we outlined the different stages in GLAD epitaxial growth. Of course, a complete theory of GLAD nanowire-epitaxy will need to involve the effect of the chemical bonding mismatch at the film–substrate interface, and the deposition parameters, more importantly, the temperature and the deposition angle. We encourage further experimental and theoretical studies on these issues.

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