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Successful and unexpected epitaxial growth of Cu/CaF_2 bilayers on hydrogen terminated Si(111) wafers by thermal evaporation is reported. The bilayers were characterized with conventional x-ray diffraction experiments, grazing angle incidence x-ray diffraction experiments, rocking curves, and χ scans. The growth mode of Cu films on CaF_2 epitaxially grown on Si(111) is completely different from that of the Cu film grown directly on Si(111). © *1995 American Institute of Physics.*

The growth of epitaxial thin films has been of great interest in recent decades. The studies of the thin film interactions between metals and insulators, as well as between metals and semiconductors, have long been explored with both scientific and technological interests.[1]

Very recently, studies of epitaxial growth of Cu on single-crystal Si wafers have shown that for Cu(100) thin films epitaxially grown on Si(100), there occurs a 45° rotation of the Cu(100) lattice relative to the Si lattice,[2] while for the epitaxial growth of Cu films with the (111) orientation, there occurs a 30° rotation of the Cu(111) lattice relative to the Si lattice. The presence of a copper silicide at the Cu–Si interface[3] has been used to explain these experimental findings.

The epitaxial growth of thin films of CaF_2 on silicon is fairly well known.[4] Li *et al.*[5] have reported on the growth of epitaxial GaAs thin films on CaF_2(111)/Si(111); Kiselev *et al.*[6] presented epitaxial heterostructures of Si and CaF_2 on Si(100); Watanabe *et al.*[7] have shown the epitaxial heterosystem growth with nanometer-thick $CoSi_2$ on CaF_2(111)/Si(111) and Suemasu *et al.*[8] have shown its application in a metal–insulator resonant tunneling diode. However, the first work to our knowledge of epitaxial growth of metals (Fe/Cu multilayer) on CaF_2(111)/Si(111) was reported by Durand *et al.*[9] It is important to emphasize that all works mentioned above were done using MBE systems.

In this communication, we now report the formation of single-crystal Cu films grown on epitaxial CaF_2/Si(111) using electron-beam evaporation and characterized by different x-ray diffraction techniques.

The bilayer thin films were deposited on bare commercial HF-etched Si(111) wafers, which have an angle of 2.5° between the surface and the Si(111) planes, in a double e-beam BALZERS UMS 500P system. The base pressure before deposition was 2×10^{-8} mbar. CaF_2 (400 Å) was deposited at 400 °C with a deposition rate of 1 Å/s. After the deposition, the CaF_2 film was submitted to *in situ* rapid thermal annealing of 1000 °C for 1 min, using a halogen lamp. The substrate temperature was measured with a chromel-constantan thermocouple. The Si substrates were then allowed to cool to room temperature and Cu(300 Å) was deposited at 1 Å/s, with no intentional heating of the substrates during deposition.

The orientation of the bilayer in the direction perpendicular to the film plane was analyzed by conventional x-ray diffraction in a Bragg–Brentano geometry and grazing angle incidence x-ray diffraction in an asymmetric geometry, both with Cu K_α radiation. The crystalline quality of the Cu films was analyzed using the rocking curve technique in double-crystal geometry with Cu K_α line radiation and a (111) oriented Si single crystal as the first crystal.[10] To investigate the epitaxial relationships in directions parallel to the interfaces of the CaF_2 film grown on Si(111) and the Cu film grown on the CaF_2 film, we used the χ scan in grazing incidence diffractometry (GID) with a geometry similar to Segmüller's,[11] using Cu K_α line radiation and a Ge(111) monochromator.

The orientation of the bilayer was first investigated with the conventional x-ray θ–2θ diffraction as shown in Fig. 1. This figure shows the first evidence of the Cu film epitaxy, where it is seen that, besides the substrate peaks, only the Cu(111) diffraction line is present. The CaF_2 lines are not detectable due to the complete match of the CaF_2 and Si lattices.

The GID χ scan to the Si(220) planes, shown in Fig. 2 is evidence of the presence of the CaF_2 film and reveals it to be epitaxied on Si(111) with *A*-type epitaxy.[12] In the GID χ scans exists a geometric dependence of the intensity ratio between substrate and film peaks with the grazing incidence angle (α), on small variations of the χ angle. However, a misalignment angle between the surface of the substrate and Si(111) planes produces a change in intensity of the peaks in the χ scans. The grazing incidence angle evolves when the sample rotates with respect to its ⟨111⟩ axis.

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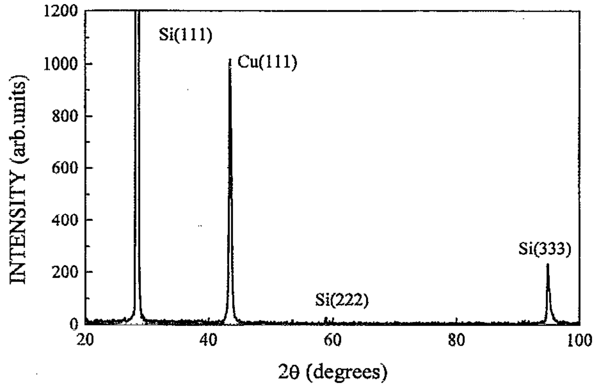

FIG. 1. X-ray diffraction pattern in Bragg–Brentano geometry of a Cu (300 Å)/CaF_2 (400 Å) bilayer deposited on hydrogen terminated Si(111) by evaporation.

TABLE I. Intensities and full width at half maximum of the rocking curves in double-crystal geometry with Cu K_α line radiation and using a single crystal of Si(111) as the first crystal.

Sample	Peak intensity (arb unit)	FWHM (arcsec)
Si(111) wafer	37 519	13.37
CaF_2/Si(111)	22 306	16.40
Cu(111) film	738	8568
Cu(111) by kinematic theory	⋯	1033

Table I shows the rocking curve experimental results. We compare the full width at half maximum (FWHM) of CaF_2/Si(111) with a bare area of the Si(111) wafer FWHM. The very small difference indicates a low level of strain in the CaF_2 layer. For a CaF_2 film of 1000 Å grown on Si(111), Singh *et al.*[13] report a much larger FWHM. This indicates that CaF_2 films grown on silicon by evaporation at low temperatures with after *in situ* rapid thermal annealing are of very good quality. Lattice distortion due to the Cu/CaF_2 interface on the CaF_2 film is believed to have a negligible effect due to the softness of the metallic binding compared to the ionic binding. This fact is directly related to physical constants of materials. For a physical example, the ratio between the Young's modulus in the [110] direction of CaF_2 and Cu is 28.8 while between Si and CaF_2 it is 2.3.[10,14,15] The Cu(111) rocking curve reveals a large value for the FWHM in comparison with the value obtained by our kinematic theory calculations for a perfect single crystal of Cu(111) 300 Å thick. We attribute this difference to two reasons: the existence of planar twins, verified by asymmetric scans in grazing angle incidence, as in the Ge/CaF_2/Si(111)[16] case, and the presence of misfit dislocations. The lattice misfit is −33.8% between CaF_2 and Cu; however, a coincidence lattice misfit can originate a much lower misfit.[17] In our case, the lowest coincidence lattice misfit in the Cu/CaF_2 epitaxial system occurs when three Cu atom spacings differ from two Ca atom spacings by approximately 0.74%. A similar situation is observed in epitaxial growth of TiN films on Si(100),[18] where the TiN films show a high density of misfit dislocations.

Figure 3 shows the GID χ scan results scanning with the detector in $2\theta=47°$ and $2\theta=75°$ to analyze the Si(220)+CaF_2(220) and Cu(220) planes, respectively. In this figure, one observes the influence of α angle variation on the intensity of the peaks. Due to geometric factors in the GID χ scan, we can conclude that since the angular separation between consecutive Cu(220) and CaF_2(220) peaks is equal to the difference between the respective Bragg angles, then no rotation occurs between the Cu(111) and CaF_2(111) lattices with respect to the interface normal. Figure 3 shows that the difference is around 14° while the difference between the Bragg angles of Cu(220) and CaF_2(220) planes is 13.77°. Clearly, no rotation is observed between the Cu and CaF_2 lattices about the ⟨111⟩ axis. This growth mode reported here is definitely different from the epitaxial growth of Cu films directly on Si(111) wafers, where a silicide layer reduces the interfacial free energy and accommodates the Cu–Si mismatch by 30° in-plane rotation.[3] Probably, the growth mode of Cu on CaF_2(111) is similar to the growth mode of Ag epitaxial films on Si(111),[19] where no reaction occurs at the interfaces. In the cases where compound formation is absent, surface structures have been determined and used to explain the epitaxy.[20]

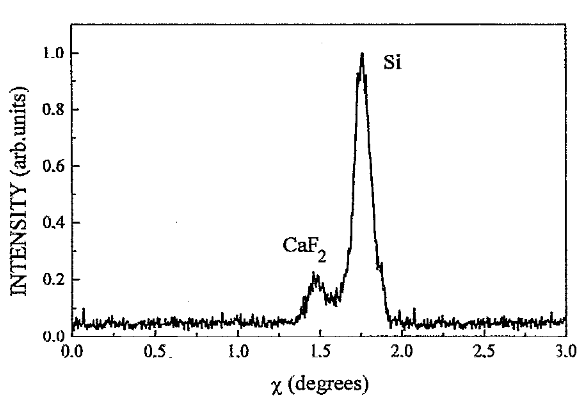

FIG. 2. Grazing incidence diffractometry χ scan of Si (220) planes ($2\theta=47°$) with grazing incidence angle $\alpha=1.3°$.

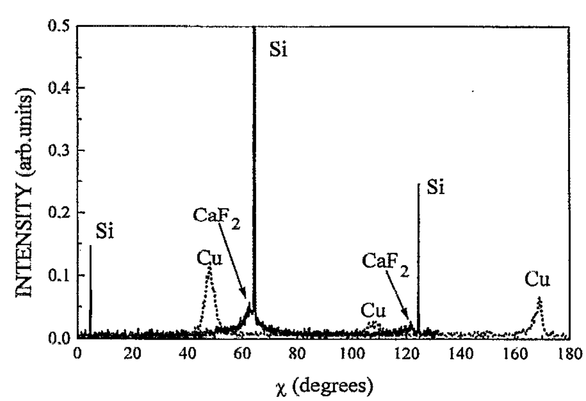

FIG. 3. Grazing incidence diffractometry χ scan of (solid line) Si (220) planes ($2\theta=47°$) and (dotted line) Cu (220) planes ($2\theta=75°$). Both the GID χ scans were performed with $\alpha=1.9°$ for $\chi=0°$.

In conclusion, we have observed surprisingly high quality epitaxial growth of evaporated Cu(111) films on evaporated epitaxial layers on CaF_2(111) grown on Si(111) using different x-ray diffraction techniques. The growth mode of Cu films on CaF_2(111)/Si(111) is definitely different from the growth mode of Cu films on Si(111), since the Cu films grown on CaF_2(111)/Si(111) have not shown evidence of rotation about the surface normal and the CaF_2 epitaxial layer prevents reaction between Cu and Si in as-deposited samples.

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