X-ray pole-figure study of the epitaxial growth of C₆₀ thin films on mica (001)

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Abstract. The growth of epitaxial C₆₀ thin films on mica(001) by thermal evaporation has been studied in detail by X-ray pole-figure measurements. The influence of the deposition rate, the substrate temperature and the film thickness on the in-plane epitaxial arrangements and the formation of twins has been investigated. It has been demonstrated that the C₆₀ growth is determined by two independent and equivalent C₆₀-crystal grain alignments (type-A and type-B). The nearly six-fold symmetry of the mica(001)-substrate surface offers the three-fold fcc-(111)-oriented C₆₀-crystal grains two equivalent crystal alignments. A high deposition rate of 0.5 Å/s is responsible for the formation of twins at a substrate temperature of 150 °C, which diminishes by a higher substrate temperature of 200 °C. By a decrease of the deposition rate down to 0.08 Å/s the twins vanish at a film thickness of 200 nm and at the substrate temperature of 150 °C. Under the same sublimation conditions, in addition to the type-A and type-B crystal orientations, the growth of the thin C₆₀ films starts with a slight fibre texture which does not appear at a larger film thickness.

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The investigation of the physical properties of thin C₆₀ films grown on different substrates is of fundamental scientific interest and also important with regard to possible future technical applications [1]. Numerous studies of the growth of C₆₀ thin films on different substrates have been performed with the aim of getting epitaxial ordering between the substrate and the C₆₀ film, increased grain sizes of the crystal of nearly 1 μm and getting a complete layer without hillhocks or holes. The good film quality is crucial for further experiments on C₆₀ thin films, for example, considering diffusion and transport properties, which are associated with the granular morphology of the thin film. Various substrates as mica [2], MoS₂[3], GeS[4], Si[5], CaF₂[6], GaAs[7] and GaSb/Sb multilayers [8] are used to obtain epitaxial thin films, but mostly the grain sizes of the thin films are strongly limited to the order of ten angstroms. Up to now, mica and GeS are well known as the substrates with the best growth properties. In comparison to GeS(001), mica (001) has the disadvantage of a lattice misfit of 3.4%. On the other hand, mica is frequently used as a substrate, because it can be cleaved easily resulting in large areas of atomically flat surfaces. On mica(001), the initial growth starts with isolated islands [9]; the size and the shape of the C₆₀ islands strongly depend on the substrate temperature [10]. Above a critical film thickness, a non-ideal layer-by-layer growth starts which has led to a complete C₆₀ layer at a film thickness of 250 nm and at certain deposition-process conditions [10].

The conventional technique for growing thin C₆₀ films is physical vapor deposition. This technique allows to control independently from each other the deposition rate and the substrate temperature and thus the study of the growth process. On mica(001), ordered (111)-oriented C₆₀ films are grown by this technique using a low deposition rate of 0.25 Å/s and a substrate temperature between 100 and 150 °C. At a film thickness of 50 nm, an increase of the substrate temperature up to 200 °C leads to a nearly perfect crystalline morphology observed by transmission electron microscopy [11]. But an additional increase of the film thickness up to 250 nm results in a significant decrease of the film quality. To enhance epitaxial ordering, alternatively also the hot-wall method is used to grow so-called pseudo-epitaxial thin films which have been characterized by X-ray diffraction and have shown an in-plane mosaic spread of 0.9° and an in-plane correlation length of nearly 450 Å at growth rates of 0.25 Å/s and thicknesses between 100 and 200 nm [12]. An increase of the growth rate up to 1 Å/s or 2 Å/s using an effusion cell has facilitated the oriented growth of μm-thick C₆₀ sheets, but the quality of the out-of-plane mosaic spread and the in-plane epitaxial arrangement of the μm-thick C₆₀ sheets has reduced [13]. It could be shown recently by X-ray diffraction experiments that 250 nm oriented thick C₆₀ films grown by conventional physical vapor deposition at a deposition rate of 0.5 Å/s reach a minimal out-of-plane mosaic spread Δθ = 0.2° (resolution: 0.1°) at a substrate...
temperature of 150°C and, in comparison, a minimal in-plane azimuthal spread $\Delta \phi = 0.74^\circ$ at an increased substrate temperature of 200°C [14].

Starting from the earlier described [14] epitaxial growth parameters, in this paper, the growth of epitaxial $\text{C}_6\text{O}$ thin films is described by using X-ray pole-figure measurements. In pole figures not only $\text{C}_6\text{O}$ crystals with $(hkl)$-lattice planes parallel to the substrate surface as in conventional X-ray $\theta$–$2\theta$-diffraction experiments are resolved, but also the $[hkl]$-directions of the $\text{C}_6\text{O}$ crystals which are inclined to the substrate surface, e.g., the $[111]$-directions which are inclined with an angle of $70.5^\circ$ to each other. Therefore, additionally, the interfacial orientational alignments between the $(111)$-oriented $\text{C}_6\text{O}$-crystal grains and the mica$(001)$ substrate may be studied. In the present paper, the quality of the epitaxially aligned $\text{C}_6\text{O}$ thin films is characterized by the interfacial orientational alignments between the $\text{C}_6\text{O}$-crystal grains and the mica$(001)$ substrate. We point out that this quality strongly depends on the growth parameters as (i) deposition rate, (ii) substrate temperature and (iii) film thickness.

1 Sample preparation and experimental setup

$\text{C}_6\text{O}$ microcrystalline powders synthesized with a purity of 99.9% and filled in a Ta crucible were used for conventional thermal evaporation in a stainless-steel vacuum chamber. A vacuum of $10^{-6}$ Torr is achieved by pumping with a turbomolecular pump under sublimation conditions. The heater temperature controlled by a thermocouple placed directly on the Ta crucible and the amount of the $\text{C}_6\text{O}$ material used as source material were the parameters for changing the deposition rate. Two different deposition rates, a high one 0.5 A/s and a low one 0.08 A/s, were chosen for the thermal evaporation on mica$(001)$. The film thickness was measured by a water-cooled quartz-microbalance thickness monitor placed directly next to the substrate holder. The mica substrate is of the basic monoclinic muscovite-$1\text{M}$ type [KAl$_2$Si$_3$O$_10$(OH)$_2$] with the lattice parameters $a = 0.5208$ nm, $b = 0.8995$ nm, $c = 1.0275$ nm and the angle $\beta = 101.275^\circ$. The $(001)$mica mosaic scan shows sharp maxima with a FWHM (Full Width at Half Maximum) of 0.1°. The mica substrates were cleaved in air and then preheated in vacuum at 200°C for 12 h to decontaminate their surfaces. In this study, the substrate temperature was varied between 150 and 200°C and, additionally, the film thickness between 100 and 250 nm.

To investigate in detail the growth process of the $\text{C}_6\text{O}$ layers on mica$(001)$, the characterization was performed with a four-circle X-ray diffraction goniometer. For the X-ray diffraction measurements a Cu-X-ray tube and a graphite monochromator were used. The diameter of the incident radiation passing through a pinhole aperture was nearly 1 mm. The diffracted beam has gone through a set of collimating slits before entering the detector. For texture analysis the following adjustment of the experimental parameters were chosen: 110° integration time per step, 2° step width in both azimuthal and polar-angle directions. The absolute intensity was corrected by subtraction of the background intensity. The azimuthal FWHM $\Delta \phi$ is measured at the polar angle $\chi = 70.5^\circ$ with 0.1° step width in $\phi$ and also an integration time of 110 s. The resolution in $\Delta \phi$ is 0.3°, which is limited by the horizontal divergence of the incident radiation. For the present X-ray $(111)$-pole-figure measurements, the detector was kept fixed at a $2\theta_{hkl}$ position of 10.81°.

2 Experimental results

2.1 Orientational alignment between the $\text{C}_6\text{O}$-crystal grains and mica $(001)$

The in-plane epitaxial arrangements were examined by monitoring the $\text{C}_6\text{O}$ <111> reflections, which could be measured by inclining the $\text{C}_6\text{O}$ thin film about an axis parallel to the substrate surface, the polar angle $\chi$, from the start position at $\chi = 0^\circ$ and $\phi = 0^\circ$ ($\theta$–$2\theta$ Bragg geometry) to $\chi = 70.5^\circ$. Then, the $\text{C}_6\text{O}$ film is rotated about the sample-surface normal, the azimuthal angle $\phi$, until one of the possible <111>-directions is identical with the direction of the scattering vector.

A typical $(111)$-pole figure of a 250 nm thick $\text{C}_6\text{O}$ film grown on mica$(001)$ is shown in Figs. 1a, b. In Fig. 1a the

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**Fig. 1a, b.** $(111)$-pole figure of a 250 nm thick $\text{C}_6\text{O}$ film grown at a substrate temperature of 150°C and a deposition rate of 0.5 A/s within the $\chi$-range from 32 to 82° illustrated by (a) an intensity plot and (b) a contour plot (contour levels: 20, 10, 2)