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Epitaxial Growth of (001) Al on (111) Si by Vapor Deposition

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Epitaxial Growth of (001) Al on (111) Si by Vapor Deposition

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Abstract

Heteroepitaxial growth of (001) Al thin films on Si (111) single crystal substrates by vapor deposition was studied by means of X-ray diffraction (XRD), Rutherford back scattering (RBS) spectrometry and transmission electron microscopy (TEM) techniques. It was observed that the films deposited at room temperature exhibit random (111) texture, while the films deposited at 280°C show perfect epitaxial alignment of (001) Al planes with (111) Si planes. In the interface plane <110> close packed directions in both the film and the substrate are parallel and hence Al grows with three orientation variants in a unique mazed tricrystal arrangement.

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Despite its very large mismatch with silicon (~ 25%), Al has been found to grow epitaxially on single crystal Si substrates.\textsuperscript{1-7} However, epitaxial orientation relationships between Al and Si depend upon the conditions of growth and the substrate orientation. For example, on (111) Si substrates it is generally found that Al grows with a (111) texture at room temperature (RT), often with parallel epitaxy, i.e., in a cube-cube orientation relationship. The best-quality films of (111) Al on (111) Si have been grown by ionized cluster beam (ICB)\textsuperscript{8}, molecular beam epitaxy (MBE)\textsuperscript{7} and chemical vapor deposition (CVD)\textsuperscript{5} techniques. Even vapor deposition at RT leads to near-single crystal films of (111) Al in parallel epitaxy with a small component of (001) texture.\textsuperscript{2} In a recent communication we have shown that this (001) component can be enhanced to form films with a unique mazel tricrystal arrangement.\textsuperscript{9} For higher substrate temperatures, the (001) texture component is generally found to depend upon the growth temperatures and techniques.\textsuperscript{10, 11} However, the film growth reverts back to (111) texture above certain critical substrate temperatures which again seem to depend upon the growth techniques.\textsuperscript{1, 11} In this letter, we present a detailed examination on the epitaxial relationships, structure and morphology of the (001) Al films deposited on Si (111).

The Si substrates used in the present study were of p-type with a resistivity of about 3-21 $\Omega$cm. A small piece of size 1.25 x 1.5 cm was cleaved from a 3-inch wafer and oxidized in a solution of 1:1 by volume of H$_2$O$_2$ and H$_2$SO$_4$ for about 10 minutes followed by a deionized water rinse. Then the wafer was etched in a solution of 1:10 by volume HF and water for 10 minutes and immediately loaded into a vacuum system and evacuated to a base pressure of 2 x 10^{-7} mbar. Al films of thickness 100-300 nm were deposited from an Al charge of 5-9 purity on substrates held between RT and 300°C during deposition. At approximately 100 nm/sec, the deposition rate was exceedingly high compared to other thin film growth techniques. The texture of the as-deposited films was characterized by XRD, and the epitaxial alignment and in-plane orientation were examined by TEM in plan-view and cross-section. RBS spectra were recorded for these films to evaluate the film quality and film alignment with the substrate. Plan-view TEM samples were prepared by cutting out 3 mm discs, mechanical dimpling down to less than 5 $\mu$m and Ar ion milling at very low angle to electron transparency. The cross-sectional samples were prepared using the method described by Bravman and Sinclair.\textsuperscript{12}

A typical XRD pattern obtained from the Al film deposited on Si (111) at RT is shown in Fig. 1a. The pattern exhibits a strong (111) Al peak besides the (111) Si substrate peak, indicating that Al has a strong (111) (fiber) texture. However, when the substrate temperature was increased (001)-oriented Al grains appeared in addition to the (111) texture. For a substrate kept at 280°C for
4 hrs before deposition, the Al film shows a pronounced (001) texture with a small amount of (111) component as illustrated in the XRD pattern, Fig. 1b.

As a complement to the X-ray data, electron diffraction was employed to check the in-plane orientation of the Al with Si. Fig. 2a shows an electron diffraction pattern obtained from a region of Al and Si for a film deposited at RT. A (220) Al polycrystalline ring pattern is seen superimposed on a strong hexagonal array of spots from the (111) Si substrate, indicating that this film has a (111) (fiber) texture with random in-plane arrangement. In contrast, the film deposited at 280°C gave rise to a perfect epitaxial electron diffraction pattern as shown in Fig. 2b, indicative of complete in-plane alignment of Al. Although double diffraction leads to a complex array of diffraction spots in this pattern the epitaxial alignment is clearly apparent from the super-imposed three (001) patterns (marked by squares) on the (111) Si pattern (outlined by a hexagon). The orientation relationship (OR) between the thin film and the substrate can be deduced from Fig. 2b as one in which the close packed <110> directions in both crystals are parallel in the interface plane, while the (001) planes of Al are parallel to the (111) surface of the Si substrate:

\[(001)_{\text{Al}} \parallel (111)_{\text{Si}}\]
\[\{110\}_{\text{Al}} \parallel \{110\}_{\text{Si}}\]

There are three orientation variants of the (001) Al pattern as observed in Fig. 2b because there are three equivalent ways of orienting (001) Al on (111) Si in such a way that the close packed directions are aligned. This is illustrated schematically in Fig. 3a. Fig. 3b shows a diffraction pattern of an Al thin film obtained from a region where the Si substrate was removed. The six-fold pattern of the Si along with its double diffraction is now missing and it is much easier to recognize the three orientation variants of the Al film which are again outlined by squares. The three patterns are related to each other by 120° rotations. However, because each pattern itself has four-fold (90°) rotational symmetry, this is identical to a 30° misorientation between variants. It can be also shown that this composite pattern has additional mirror symmetries. The point group symmetry of the whole pattern and hence the microstructure, belongs to a non-crystallographic point group, 12mm. The crystallography and morphology of this interesting tricrystal microstructure were discussed in other work.\(^{13}\)

In Fig. 4 the tricrystal microstructure is shown in three dark-field images recorded from the same area with the (200) reflections of each variant. The three orientation variants cover almost the entire area. A tracing of the three dark field images, seen in Fig. 4d with each orientation variant characterized by different shading shows that the three grain orientations form an interlocking jig-
saw puzzle structure with both dual and triple facet junctions. Only a few small grains remain unshaded in this tracing. These grains were in the minority (111) orientation, also detected by XRD, and their volume fraction was small. Although perhaps not immediately apparent from Fig. 4, this mazed tricrystal microstructure is unique. Because all the grains are related to each other by 120° (or 30°) rotation, the misorientation is identical across any of the grain boundaries. Although each boundary is free to take any inclination, the misorientation remains fixed through the symmetry constraints imposed by the substrate. This results in a unique geometry where triple junctions can be composed of three identical grain boundaries.\textsuperscript{13}

The quality of epitaxial alignment between Al (001) and Si (111) was examined by He\textsuperscript{+} ion channeling with an incident energy of 2 MeV. The spectra of the backscattered He\textsuperscript{+} ions were recorded at a scattering angle of 165°. Fig. 5 shows the random and aligned (along the Si <111> axis) spectra obtained from an Al (001)/Si (111) film. The spectra seen in the higher energy side is from the Al film and the lower energy part is from the Si substrate. From the known data of He\textsuperscript{+} energy loss in Al, the thickness of the Al film was deduced to be 190 nm. The minimum He\textsuperscript{+} scattering yield $\chi_{\text{min}}$ near the surface peak was determined to be 13% compared to ~6% for a single crystal. This result indicates that the film quality in the present investigation compares favorably with that achieved by other techniques.\textsuperscript{3,14}

The structure of the Al/Si interface was investigated directly in cross-sections prepared from these samples. Fig. 6a shows a conventional electron micrograph of a Al (001)/Si (111) interface in cross-section. The film thickness was measured to be about 200 nm, in good agreement with the RBS data. The grain size was between 200 and 1000 nm. It is interesting to note that the grain boundaries are nearly perpendicular to the interface. The interface appears to be flat in the low resolution micrograph. However, close examination at high resolution (Fig. 6b) reveals that the interface consists of areas with perfect epitaxy separated by amorphous pockets of size 1-2 nm. The epitaxial alignment of the Al lattice with the Si along the closed packed <110> directions (perpendicular to the plane of Fig. 6b) is excellent as also revealed by the RBS spectra shown in Fig. 5. As observed for the Al (011)/Si (100) system, these amorphous pockets were found to be abundant in the interface.\textsuperscript{15} It is concluded that nucleation occurs at pin holes where the epitaxy is perfect and during subsequent growth the film covers the oxide islands. Where the growing Al grains of different variants impinge they form 30° <001> tilt grain boundaries.

The epitaxial orientation relationship observed in the present experiments is commonly found in the heteroepitaxial growth of thin films for a variety of growth techniques\textsuperscript{1,2,6,10,11} and in
the topotaxial growth of precipitates.\textsuperscript{16} Although in all cases examined this orientation relationship appears to be exact, it is not predicted by any of the simple crystallographic criteria based on the near-coincidence-site concept. It is rather unexpected to observe a strong (001) texture on Si (111) at this substrate temperature since geometrical lattice matching would only predict the cube-cube epitaxy.\textsuperscript{9} Whether its occurrence is related to kinetic, structural, crystallographic or chemical criteria is still subject to investigation.

In summary, we have shown that a high quality Al (001) thin films can be grown on Si (111) by a simple physical vapor deposition method. Due to a heteroepitaxial orientation relationship grains form in three symmetry related (001) orientations. Though this epitaxy is not predicted by the geometric criteria based on lattice mismatch, high quality films form in perfect epitaxial alignment with the substrate.

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References

Figure Captions

Fig. 1 X-ray diffraction patterns showing the evolution of texture in Al thin films deposited on (111) Si substrates. (a) room temperature deposited film shows only a strong (111) peak and (b) film deposited on substrates held at 280°C for 4 hrs shows a strong (002) peak besides a minor (111) peak.

Fig. 2 Selected area diffraction patterns illustrating the in-plane orientation of Al films on Si (111). (a) room temperature deposition shows a random (111) texture and (b) deposition after holding the substrate at 280°C for 4 hrs results in pronounced (001) texture, with only three orientation variants in the plane rotated by 120° relative to each other.

Fig. 3 (a) Schematic illustration of the three Al variants marked 1, 2 and 3 of the observed orientation relationship with Si (111) and (b) the tricrystal electron diffraction pattern from the free standing Al after removing the substrate. The three variants are marked by squares.

Fig. 4 Dark field electron micrographs of the three orientation variants of Al (001) grains (a)-(c) illustrate the tricrystal microstructure. The schematic in (d) shows the interlocking distribution of the three variants of (001) grains and the white areas represent remaining grains in the minority (111) orientation.

Fig. 5 Random and aligned (marked) RBS spectra recorded from a Al (001)/Si (111) sample with 2 MeV He⁺ ions.

Fig. 6 (a) Low magnification cross section micrograph of Al (001)/Si (111) sample shows a planar interface and grain boundaries nearly perpendicular to the interface. (b) High resolution image of the interface shows the presence of amorphous pockets and pin holes where the epitaxy is perfect.
Figure 1

(a) Al/Si(111) RT (32°C)

(b) Al/Si(111) 4h @ 280°C
Figure 5