Comment on “Dimensionally Induced Structural Transformations in Titanium-Aluminum Multilayers”

Banerjee, Ahuja, and Fraser reported [1] face-centered cubic (fcc) Ti and hexagonal close-packed (hcp) Al in as-deposited Ti/Al multilayers with nm-scale composition modulation wavelengths (CMW). As the equilibrium bulk forms of Ti and Al are hcp and fcc, respectively, these novel results warrant careful scrutiny. Transmission electron microscopy/diffraction (TEM/ED) artifacts in Ti/Al multilayers with large CMW have been noted previously [2]. We therefore comprehensively studied Ti/Al multilayers with 7.2 and 5.2 nm CMW [3] by x-ray diffraction (XRD) and TEM/ED to address this important issue. Specimens were prepared by electron beam evaporation in high vacuum (10^{-6} Pa during deposition) on water-cooled Si wafers and examined by reflection and transmission XRD. Thin foils were then prepared for high resolution (HR) TEM/ED. Our results clearly demonstrate that the Ti in these multilayers deposits as hcp and that fcc Ti is merely an artifact of producing specimens for cross-sectional TEM. Moreover, no evidence was found to support claims [1] of hcp Al either by XRD or TEM/ED.

Figure 1 shows θ-2θ reflection XRD data of the *as-deposited* 5.2 nm CMW multilayer film as well as the digitized intensity in the [111] direction of a [112] zone ED pattern, both versus the scattering vector k_s in the [111] (growth) direction. The closely matched $(00.2)_{\text{Ti-hcp}}$ and $(111)_{\text{Al-fcc}}$ plane spacings of the highly textured films result in a single XRD peak (at 4.31 nm^{-1}) even for nm-scale CMW. The $(111)_{\text{Ti-fcc}}$ XRD peak is clearly absent. In contrast, ED peaks for the $(111)_{\text{fcc}}$ Ti and Al layers are visible. CMW satellites along the growth direction are visible in both profiles. Figure 2 shows the 5.2 nm CMW multilayer [110] zone by HRTEM (raw image, no Fourier filtering). The common growth direction is [111] (vertical), and the Ti and Al layers both exhibit the characteristic fcc stacking sequence, *abcabc*. Lattice parameters for the Ti and Al are 0.44 and 0.41 nm, respectively. XRD/TEM results for the 7.2 nm CMW are essentially identical to those from the 5.2 nm CMW, aside from smaller satellite spacing.

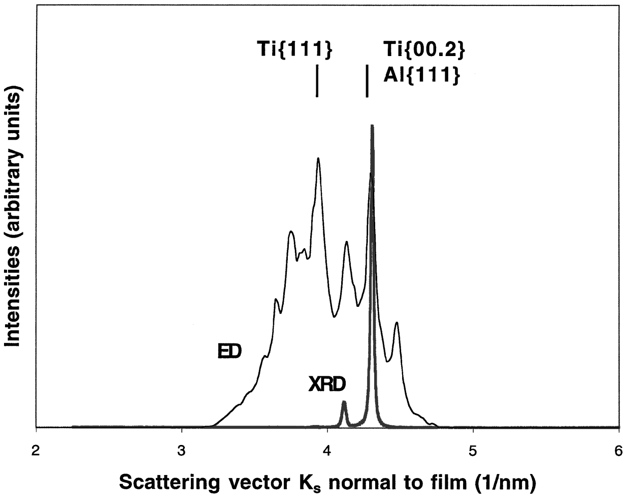

FIG. 1. Intensity of (111) diffraction spots and satellites from 5.2 nm CMW. XRD (grey) and TED (solid) profiles indicate fcc Al and the CMW. The $(111)_{\text{Ti-fcc}}$ diffraction peak is present only in the TEM-prepared specimen.

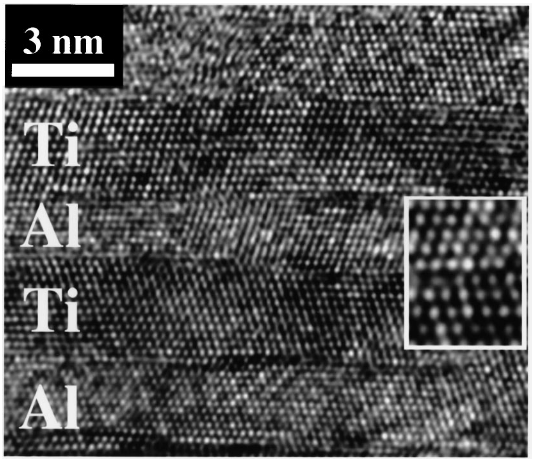

FIG. 2. Ti/Al multilayer, note *abcabc* stacking (Ref. [3]).

Banerjee, Ahuja, and Fraser [1] have observed fcc Ti and hcp Al only in Ti/Al multilayers prepared for TEM. Ion irradiation used in TEM preparation is a possible mechanism for the transformation [3], therefore determinations of deposited microstructure by TEM are potentially erroneous. The issue of whether these materials actually deposit as asserted can be resolved only through studies of as-deposited films, e.g., by high-angle XRD or neutron diffraction.

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Received 17 July 1998 [S0031-9007(99)08436-7]
PACS numbers: 61.10.Kw, 61.14.Lj, 61.16.Bg, 68.65.+g

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