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RHEED studies during growth of TiN/SiN_x/TiN trilayers on MgO(001)

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Abstract

TiN/SiN_x/TiN(001) trilayers have been deposited on MgO(001) substrates using ultra-high vacuum based reactive magnetron sputtering and studied by in situ reflection high energy electron diffraction (RHEED). Depositions were carried out at 500 °C and 800 °C, with SiN_x layer thicknesses between 3 and 300 Å. Here, we find that SiN_x(001) layers grown at 800 °C exhibit 1×4 surface reconstructions along orthogonal ⟨110⟩ directions up to a critical thickness of ~9 Å, where an amorphous phase forms. Growth of TiN overlayers on the reconstructed SiN_x(001) layers yield RHEED patterns indicating the growth of (001)-oriented epitaxial layers with a 1×1 reconstruction. For the case of amorphous SiN_x layers the TiN overlayers grow polycrystalline.

Keywords: Physical vapor deposition; Reflection high energy electron diffraction (RHEED); In situ characterization; Epitaxy; Surface relaxation and reconstructions; Phase transition; Titanium nitride; Silicon nitride

Nanoscale thin films from the Ti–Si–N system are attracting a large interest for the design of wear-resistant nanocomposites and multilayers [1–7]. It has been identified that the interfaces between TiN and stoichiometric Si_3N_4 or metastable SiN_x determines to a dominant part the mechanical strength of the materials' structure. For the case of nanocomposites, e.g., the hardness values are vastly different between studies, ranging from 30 to ~100 GPa [5–7]. Discussions regarding this spread in reported properties identifies the key parameters deposition temperature, nitrogen partial pressure, and oxygen contamination [8,9].

When deposited under conditions for optimizing mechanical hardness, TiN/SiN_x nanocomposites consist of TiN nanocrystallites encapsulated in what is assumed to be 1–2 monolayers of amorphous Si_3N_4 at the percolation threshold [7,10,11]. However, recent work suggest that the interfacial structure between TiN and SiN_x is more complex [1–4,12] than previously described, exhibiting also metastable cubic SiN [4,12] tissue phase layers. The tissue phase is strain-stabilized to TiN(001) and TiN(111) surfaces [4]. In these studies the growth of crystalline SiN interlayers with an epitaxial relationship to TiN has been observed by high resolution transmission electron microscopy. *Ab initio* calculations corroborates these findings as they yield a lattice parameter of NaCl–SiN ($a_{SiN} = 0.99 a_{TiN}$) [3,13] similar to that of TiN ($a_{TiN} = 4.242$ Å [14]). In accordance, high resolution X-ray diffraction studies of TiN/SiN_x superlattices show only strained TiN 002 peaks in addition to the MgO 002 peak [12]. Hultman et al. [4] further used in situ low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) to reveal 1×5 surface reconstructions of SiN_x(001) along ⟨110⟩ when grown onto TiN(001) template layers.

In order to further characterize the surfaces and structural evolution of the involved phases in TiN/SiN_x/TiN trilayer structures, reflection high energy electron diffraction (RHEED) studies were performed. The corresponding film

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layer depositions were carried out in an ultra-high vacuum system with a background pressure below 4×10^{-7} Pa (3×10^{-9} Torr) equipped with dual magnetrons and an in situ RHEED setup from STAIB Instruments. The main components of the residual gas were H_2 and N_2, as measured by an in situ residual gas analyzer. The background impurities in the films, such as oxygen, are thus expected to be very low. Elemental analysis performed with a CAMECA IMS6F secondary-ion-mass spectroscope during growth in the same vacuum system of a similar AlN thin film system revealed low C and O concentrations at 1.3×10^{18}, and 3.5×10^{18} cm^{-3} [15]. Targets consisted of 3 in. Ti (99.97% purity) and Si (99.99% purity) discs. Argon and nitrogen were used as working and reactive gas, respectively, and the purity of the gases was 99.999999%, obtained through the use of getter gas purifiers. During depositions the partial pressures were 4.0 mTorr and 0.5 mTorr for Ar and N_2, respectively. MgO(0 0 1) wafers with size $10 \times 10 \times 0.5$ mm^3 were used as substrates. Before insertion in the load-lock, the substrates were cleaned in consecutive ultrasonic baths of trichloroethylene, acetone, and isopropanol. Prior to deposition, the substrates were preheated in situ for at least 1 h at 800 °C to outgas and anneal the substrate surface. Thereafter the TiN template layers were deposited, at a substrate temperature of 800 °C. The sandwiched SiN_x layers and the TiN overlayers were then deposited at 500 °C or 800 °C. TiN layer thicknesses were kept constant throughout the depositions at 300 Å and 500 Å for the template and overlayers, respectively. The experimental geometry with a graphite sample holder allowed for RHEED observation along the zone axes [0 1 0] and [1 1 0] during growth. A RHEED electron gun with accelerating voltage 35 kV was used at an incident electron beam angle of ~1°. The reflected electron diffraction pattern, as formed on a fluorescent screen, was captured by a 12 bit CCD camera. The image files were imported into MATLAB where the pixel intensity along the vertical directions were summed up and thereafter plotted against the horizontal pixel positions, thereby producing projected intensity curves.

Fig. 1 shows RHEED patterns and the corresponding intensity curves from a typical TiN(0 0 1) template layer surface, (a) and (c) are viewed along the [0 1 0] zone axis (Z.A.), whereas (b) and (d) are viewed along [1 1 0]. Marked are the fundamental streaks originating from the intersection of the reciprocal lattice rods, which constitute the reciprocal description of a thin surface, with the Ewald sphere. For MgO and TiN, both with the NaCl-type lattice with sample edges along [1 0 0] and [0 1 0], and a surface normal along [0 0 1], the surface unit cell is spanned by the vectors $\mathbf{s}_1 = a/2 \cdot [1\,{-1}\,0]$ and $\mathbf{s}_2 = a/2 \cdot [1\,1\,0]$, where a equals the bulk lattice parameter. The notations in the figures corresponds to the reciprocal surface vectors $\mathbf{s}_1^*$ and $\mathbf{s}_2^*$. In the case of an ideally flat surface, points should be seen. However, well-defined streaks like the ones observed in Fig. 1a and b suggest a flat single-crystal surface with surface terraces and steps. The streaks are thin, indicating large coherently scattering regions perpendicular to the incident beam [16–18]. No transmission pattern is observed, which indicates that the surface is flat, i.e. without surface asperities. If the brightness is increased, additional fundamental streaks, and also Kikuchi lines, were observed. The findings from Fig. 1 are consistent with a 1×1 reconstructed TiN(0 0 1) template grown epitaxially

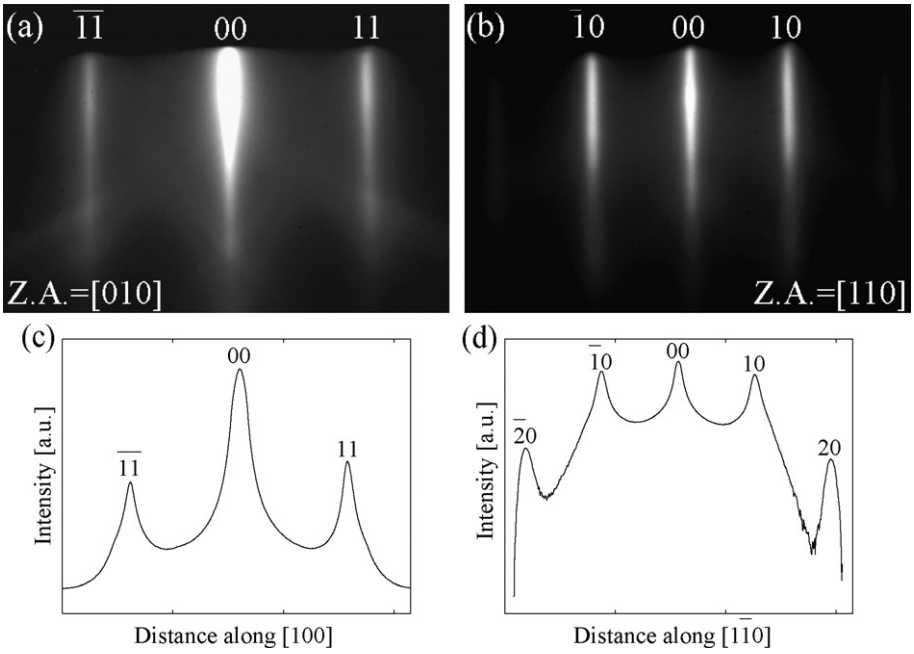

Fig. 1. RHEED patterns and intensity curves from a single-crystal TiN(0 0 1) film grown on MgO(0 0 1) at 800 °C. (a) and (c) along zone axis (Z.A.) [0 1 0] and (b) and (d) along Z.A. [1 1 0]. Hence, the horizontal axis in (c) and (d) is perpendicular to the respective Z.A.