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Origins of microstructure and stress gradients in nanocrystalline thin films: The role of growth parameters and self-organization

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Abstract

The development of depth gradients of texture, morphology and stresses in thin nanocrystalline films was experimentally demonstrated for a nanocrystalline CrN film by means of position-resolved synchrotron X-ray nanodiffraction and explained by atomistic processes at the growing film surface and the effect of interfaces, both controlled by the deposition conditions. Controllable changes in the energy of incident particles adjusted by bias voltages ranging from −40 to −120 V affect the competitive growth of grains with different orientations, induce disruption of grain growth and thus give rise to structural variations across the film thickness. Subsequent changes in the volume fraction of grain boundaries and film texture were found to be responsible for changes in the residual stress state as defect generation proceeds to different extents in the interior of differently oriented grains and in the interfacial area. While the defect density predominantly affects the development of intrinsic stress, the variation in the number of weakly bonded atoms of grain boundaries determines the thermal stress component. The structural dependence of both stress components thus contributes to the characteristic development of stress gradients in thin nanocrystalline films.

Keywords: Residual stress; Stress gradient; Microstructure; Film growth; Nanocrystalline films

1. Introduction

The microstructure of nanocrystalline materials has been shown to be crucial in determining their outstanding mechanical and other physical properties (e.g. electrical, magnetic or thermal), which significantly differ from those of conventional materials. The uniqueness of nanocrystalline materials is the large proportion of atoms at interfaces, which is considerably higher with respect to their coarse grained polycrystalline counterparts [1]. Many of the physical properties of such structures are, however, highly residual stress dependent, which becomes especially important in thin nanocrystalline films prepared under highly non-equilibrium conditions. These materials are typically anisotropic and under relatively large compressive stress, which particularly affects their mechanical but also other physical properties.

The macroscopic behaviour of nanocrystalline film materials corresponds to volume-averaged properties which may, however, vary significantly on the nanometre length scale. This stems from the evolutionary nature of film microstructure development due to competitive growth resulting in inhomogeneity in the crystallographic texture, composition, strain and morphology, and thus also in gradients of physical properties across the film thickness.

The thickness dependence of the film microstructure and texture has been studied in several film model systems and discussed in detail [2,3], together with the thickness-dependent

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stress state and thermal properties [4–6]. However, most of those studies focused on investigation of the thickness dependency in increasingly thick films. Although a few experiments can be found in the literature focused on variations in the film microstructure and/or residual strain/stress state with depth by X-ray diffraction (XRD) or focused ion beam (FIB) based methods [7–10], there have been no simultaneous studies of thin film microstructure, morphology and residual stress depth gradients combined within one experiment, especially in the case of complex layered thin nanocrystalline films.

In this study position-resolved wide-angle XRD analysis performed on a cross-section of a thin nanocrystalline CrN film in transmission geometry with a monochromatic beam of 250 and 100 nm diameter is used to analyse local film properties at sub-micron resolution. The main aim is to analyse and to interpret the XRD data in detail by comparing them with transmission electron microscopy (TEM) micrographs in order to obtain a general understanding of the origins of microstructure and stress evolution across nanocrystalline thin films and their dependence on the growth conditions, type of interfaces and self-organization processes.

2. Experimental details

2.1. Film deposition

The origin of structural and stress gradients in nanocrystalline films was studied by investigation of a thin CrN film prepared by unbalanced reactive d.c. magnetron sputtering (Rapid Coating System, Oerlikon Balzers) from a Cr target (99.99% purity, diameter 145 mm, Plansee Composite Materials) produced by powder metallurgy. The film was synthesized in static mode on chemically pre-cleaned Si (1 0 0) wafers with the dimensions $20 \times 7 \times 0.3$ mm mounted on a stainless steel sample holder located 20 cm from the target. While the coating chamber was evacuated to a base pressure of less than 5×10^{-4} Pa, the substrate was heated to 350 °C and subsequently sputter-etched prior to deposition in argon plasma for 20 min to remove the native surface oxide layer. The CrN film was then deposited at a constant total pressure of 1 Pa in an $Ar + N_2$ gas mixture with a nitrogen partial pressure of 0.25 Pa, target power of 6 kW and temperature of 350 °C.

Microstructure and stress profiles within the CrN film were set by changing the energy of the incident ions by means of a negative bias voltage in three steps without interrupting film growth. Each sublayer was deposited for 60 min at −40, −120 and −40 V with thicknesses of ~5 μm so that the total film thickness was 15 μm.

2.2. Film characterization using electron microscopy techniques

The microstructure of the film in cross-section and the film thickness were investigated using a Carl Zeiss Auriga scanning electron microscope and a JEOL JEM-2000FX conventional transmission electron microscope operated at 200 keV. The samples for scanning electron microscopy (SEM) and TEM investigations were prepared from representative parts of the film using an Orsay Physics Cobra Z-05 FIB apparatus. The elemental composition was determined by electron probe microanalysis by means of wavelength dispersive X-ray spectroscopy using a JEOL JXA 840 analyser under an acceleration voltage of 10 keV.

2.3. Synchrotron XRD analysis of the film

A detailed microstructural and strain state analysis of the CrN film was performed in the nanofocus extension of the ID13 beamline at the European Synchrotron Radiation Facility in Grenoble, France [11]. A slice of the film with thickness $L = 100$ μm in the beam direction was scanned in transmission geometry across the film thickness by a monochromatic X-ray beam ($E = 13$ keV) oriented parallel to the film–substrate interface (Fig. 1). For each position a charge-coupled device (CCD) area detector with a resolution of 2048×2048 pixels and a pixel size of 50×50 μm positioned behind the sample at the distance of 9.2 cm collected a Debye–Scherrer diffraction frame at a counting time of 0.5 s per frame. The size of the beam was adjusted using Kirkpatrick–Baez mirrors: (i) 250 nm in diameter to investigate development of the film microstructure; (ii) 100 nm for strain mapping at high spatial resolution. Translation of the sample in the beam along the z-axis was performed in steps matching the applied beam sizes. The two-dimensional (2-D) diffraction data were processed using the program package Fit2D [12].

3. Experimental results

3.1. Film microstructure

The microstructure of nanocrystalline films is determined by the deposition conditions under which the films grow. If a nanocrystalline film is prepared under moderate ion bombardment conditions and at a temperature close to $T_s = 0.3T_m$ its microstructure develops by competitive growth, typically with cone-like columnar grains, a high density and an evolutionary growth texture [13]. Here T_s and T_m are the deposition and melting temperatures, respectively. The final microstructure of the film is, however, also significantly affected by other parameters, such as the total pressure and the presence of a reactive gas, which were discussed in detail in Barna and Adamik [14]. In this study the partial pressure of nitrogen was carefully chosen so that the CrN film was nearly stoichiometric, with N/Cr = 1–1.09, and was exclusively composed of single phase face-centred cubic (fcc) crystal structure. In order to study the effect of the energy of incident particles and templated growth of nanocrystalline films on the development of residual stress and its relation to the film microstructure the substrate bias voltage U_s was stepwise