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Structure, stability and mechanical performance of AlN:Ag nanocomposite films

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ABSTRACT

Nanocomposite films consisting of a hard AlN matrix incorporating soft Ag inclusions (AlN:Ag) and which are suitable for protective coatings are presented. The growth has been performed using Pulsed Laser Deposition and the film structural properties, such as nanoparticle size and distribution, were studied in relation to the growth parameters, such as metal content and PLD working pressure and laser power. High resolution transmission electron microscopy and nanoindentation were employed in order to determine the film composition, inclusions' crystal structure and mechanical properties respectively. The employed Ag nanoparticles had average sizes ranging between 3–10 nm and were clearly separated by the matrix material. The critical parameters, which determine the nanoparticle size and distribution, and the decisive role of the latter on the mechanical performance of AlN:Ag nanocomposite films are established.

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1. Introduction

Aluminum nitride (AlN) is an important material for protective coatings due to its exceptional properties, such as high hardness, thermal conductivity and refractory character [1]. It has been also studied as an alloying phase in group IVb–VIb transition metal nitride-based nanocomposite superhard coatings [2–6]. The disadvantages of the use of AlN are its brittleness and its poor adhesion on various substrates [7]. The adhesion issue has been considered and resolved by growing AlN on Al interlayers [7,8]. The incorporation of noble metal nanocrystals into AlN can be employed to enhance its plasticity since besides intrinsic structural and chemical factors (e.g. bond strength), a strong effect is also imposed by deformation mechanisms such as generation and movement of dislocations and/or grain boundaries. At the same time, the dielectric character of AlN in combination with the metallic nanoparticles may add extra functionalities to these coatings [9,10]. However, the growth of such AlN-noble metal nanocomposites has not been reported yet in the literature, possibly due to the miscibility of Al into noble metals [11,12] making the Ag–AlN phase separation and the formation of nanocomposites a very difficult task; similar alloying has been also observed in Ag–Ga–N systems [13].

We present the growth and structure of stable nanocomposites based on AlN incorporating pure Ag metal nanoparticles of a very narrow size distribution. These nanocomposites consist of a hard matrix (AlN) incorporating soft inclusions (Ag); this microstructure is different from the most common nanocomposites, which consist of a softer matrix and harder inclusions. We employ transmission electron microscopy (TEM) and high resolution TEM (HRTEM) in cross-section geometry to determine the nanostructure of the coatings. In addition, the mechanical properties are evaluated by nanoidentation. We identify the parameters that determine the nanoparticles size and distribution and we show that nanoparticle size alters the mechanical performance of the coatings.

2. Experimental

Pulsed laser deposition (PLD) is a technique widely used for the growth of AlN [1,14–17]. In this work, the AlN and the AlN:Ag nanocomposite films were grown by PLD on commercial *n*-type Si (100) wafers of resistivity 1–10 Ωcm using a rotating sectored target of pure (99.999%) solid Al and Ag in a flowing N_2 ambient, following the geometry originally introduced by Wang et al. [18]. Various target geometries were employed i.e., 12.5% and 25% Ag (sectors of $2\times22.5°$, $2\times45°$ or $4\times22.5°$, as summarized in Table 1). The Si substrates were cleaned in ultrasonic baths of tetra–chloro–ethylene, acetone and methanol, rinsed by de-ionized water and dried by dry N_2 gas shower prior to deposition in order to remove organic contaminants. The native oxide was removed by chemical etching in a HF bath. The PLD growth experiments were performed in a high vacuum system (base pressure $Pb<5\times10^{-8}$ mbar). The chamber was equipped with a rotating 45 mm target and a rotating 50 mm sample holder electrically

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Table 1
List of the deposition conditions for the specimens studied in this work.

Specimen code	Target composition	Target rotation frequency (Hz)	Laser power (mJ)	Working pressure (mbar)	Deposition time (min)
A	Al 87.5%–Ag 12.5%	0.35	35	3.9×10^{-2}	30
B	Al 87.5%–Ag 12.5%	0.175	35	3.9×10^{-2}	30
C	Al 87.5%–Ag 12.5%	0.0875	35	3.9×10^{-2}	30
D	Al 75%–Ag 25% (Ag $2\times45°$)	0.035	35	3.9×10^{-2}	180
E	Al 75%–Ag 25% (Ag $4\times22.5°$)	0.035	35	3.9×10^{-2}	40
F	Al 75%–Ag 25% (Ag $4\times22.5°$)	0.035	18/35	3.9×10^{-2}	2/35
G	Al	0.35	35	3.9×10^{-2}	30

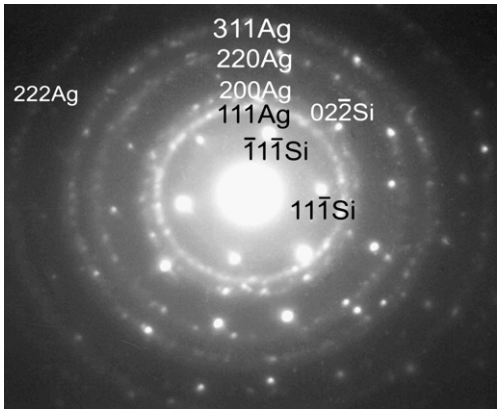

Fig. 1. SAED pattern of the AlN:Ag/(100) Si bicrystal obtained in cross-section along the [011] zone axis of silicon. The diffraction spots are coming from the Si substrate and the superimposed ring pattern corresponds to nanocrystalline relaxed Ag.

connected to a DC-power supply that was used to manipulate the kinetic energy of deposited species [19]. The target rotation frequency (TRF) was varied in the range 0.35–0.035 Hz, while the sample holder frequency was constant 0.35 Hz for all samples. The 3rd ($\lambda = 355$ nm) harmonic of a Nd:YAG laser source (pulse duration 3 ns, repetition rate 10 Hz) was used to ablate the target at room temperature (RT). The working pressure of the ablated Al vapors and flowing N_2 under these conditions varied between 1 and 80×10^{-3} mbar. A range of specimens with thicknesses from 30 up to 200 nm were studied.

The adhesion of AlN onto Si is usually poor due to the large lattice mismatch and the formation of an amorphous SiN*x* layer on the surface of the substrate. In order to avoid amorphous SiN_x, a thin (2–3 nm) interlayer of metallic Al was pre-deposited and was then exposed to pure nitrogen plasma ($P_w = 3.9\times10^{-2}$ mbar, $V_b = -450$ V) to form an AlN buffer layer. The [N]/[Al] ratio has been evaluated by *in-situ* Auger Electron Spectroscopy (AES) and it was larger than 0.9 for all samples. The AES spectra were acquired in an ultra-high vacuum (UHV) chamber ($P_b < 5\times10^{-10}$ mbar), which is connected to the PLD system through a UHV transfer line, using an electron gun (primary beam energy 3 keV) and a cylindrical mirror analyzer (CMA).

TEM studies were performed using a 200 kV JEOL 2011 high-resolution microscope (spherical aberration coefficient $C_s = 0.5$ mm, point-to-point resolution 0.19 nm). Specimens for conventional TEM (CTEM) and HRTEM observations, in cross-section (XTEM) geometry, were prepared by mechanical thinning followed by Ar^+ ion milling. The mechanical performance was investigated using a Hysitron Ubi-1 HT Tribolab modular system. Nanohardness measurements were performed with a standard Berkovich indenter tip, while qualitative information was obtained by the profile of the load-unload curves.

3. Results and discussion

The series of AlN:Ag nanocomposites studied in this work is listed in Table 1. All films have been grown at RT in order to grow amorphous AlN; amorphous III-nitrides exhibit ultra smooth surfaces, while they are retaining their high hardness values [20]. Selected-area electron diffraction (SAED) revealed that the Ag nanoparticles exhibited the *fcc* crystal structure with lattice parameter almost identical to that of pure, unstressed Ag (Fig. 1); no diffraction from crystalline AlN has been observed in SAED. The size and the filling ratio of the Ag nanoparticles inside the AlN matrix were controlled by varying the geometry (% Ag) and the TRF of the sectored target, so that a homogeneous distribution of nanoparticles could be achieved as illustrated in the TEM image of Fig. 2a. The size distribution of the Ag nanoparticles is very narrow according to the size histogram of Fig. 2b.

The target rotation frequency was found not to affect significantly the size of the nanoparticles. For the 12.5% Ag composition and with identical lasing conditions, reducing the target rotation speed resulted in average inclusion diameters 3.0 ± 0.3 nm (TRF = 0.35 Hz), 3.0 ± 0.5 nm (TRF = 0.175 Hz), and 3.2 ± 0.2 nm (TRF = 0.0875 Hz). On the other hand, the reduction of TRF was found to increase the inclusion density and hence the percentage of crystallinity in the sample; indeed, the specimen #B (12.5% Ag, $2\times22.5°$, RF = 0.175 Hz) is amorphous, while the specimen #C (12.5% Ag, $2\times22.5°$, RF = 0.0875 Hz) exhibits larger amount of crystallinity, as shown in

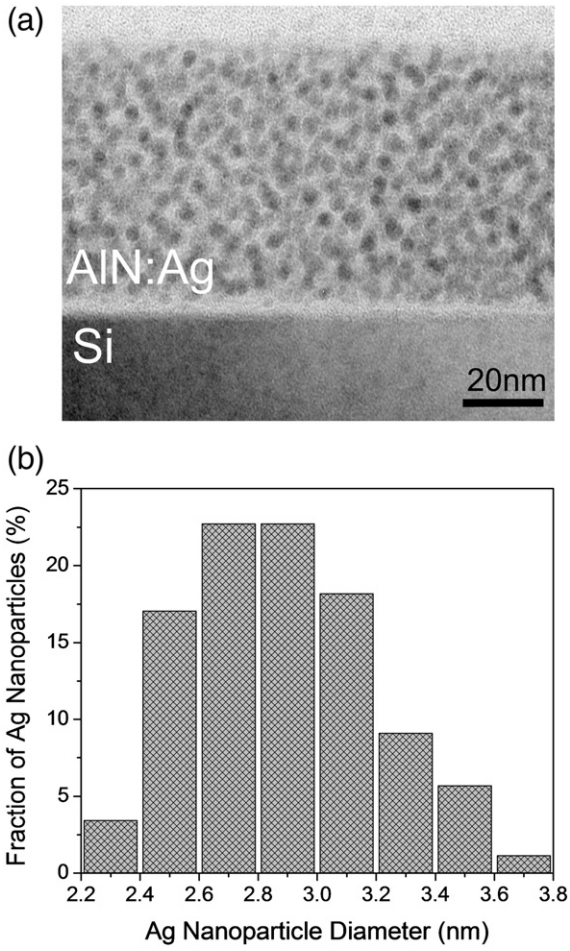

Fig. 2. (a) Cross-sectional CTEM image of specimen #E corresponding to 25% Ag and TRF = 0.035 Hz; the thickness is 48.7 nm, (b) the particle size histogram of specimen #E extracted from the CTEM image.

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