Composition and mechanical properties of AlC, AlN and AlCN thin films obtained by r.f. magnetron sputtering

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ABSTRACT

Aluminum carbide (Al–C), aluminum nitride (Al–N), and aluminum carbonitride (Al–C–N) thin films were grown onto Si [100] substrates by r.f. reactive magnetron sputtering at 400 °C. The Al–N coatings were obtained by sputtering of Al (99.9%) target in Ar/N$_2$ atmosphere and the Al–C and Al–C–N by co-sputtering of a binary (50% Al, 50% C) target in argon and in Ar/N$_2$ mixture, respectively. The d.c. bias voltage was varied between 0 and −150 V. The films were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), Fourier transformed infrared spectroscopy (FTIR) and the mechanical properties by nanoindentation. The structure of the films has been determined by XRD, which shows that amorphous films are formed in all cases. The variation of polarization bias voltage produced chemical differences in the films. As the bias voltage is increased, the Al content is reduced in all three materials. The nitrogen content also varied between 10 and 14 at.% for Al–N coatings, remaining practically constant (21 at.%) for the Al–C–N films. The Berkovich hardness results were 7.0, 17.2 and 9.2 GPa for Al–C, Al–N, and Al–C–N films, respectively.

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1. Introduction

Aluminum atoms form several structures in which aluminum is bonded to carbon, nitrogen or oxygen atoms. The simplest of these is that of AlN, which has a hexagonal structure type *wurtzite*. More complex, but related, structures are those of Al$_2$CO, Al$_4$C$_3$, and Al$_5$C$_3$N [1]. Al–C–N and Al–N thin films have attracted a great interest because of the properties that exhibit, like a wide gap, high chemical stability [2–5], and high hardness between 35 and 53 GPa for Al–C–N films [6,7] and 25 GPa for Al–N films [5]. Because of these properties, Al–C–N and Al–N films have applications in various industries including microelectronics, optolelectronics [8,9] and in pasivation of thin films, insulator layers, optical sensors in the ultraviolet and hard coatings [2–5]. On another hand, aluminum carbide, Al–C, is an important compound in the technology of aluminum and is a starting material for producing ceramics with diamond-related structure that can combine high thermal conductivity together with high electrical resistance at room temperature [10]. The synthesis of a crystalline phase of Al–C–N was first reported in 2001 using a chemical method [8]. Also Al–C–N thin films were deposited by reactive magnetron sputtering to stabilize the hypothetical β-C$_3$N$_4$ phase by the incorporation of aluminum [11]. Al–N films can be deposited by various techniques as CVD, molecular beam epitaxy and reactive magnetron sputtering [12]. However, the magnetron sputtering technique is the most used to grow Al–N films, where the microstructure of the films depends on the deposition conditions such as substrate temperature, pressure, and applied bias voltage [12,13].

In this work the effect of the d.c. bias polarization voltage on the bonding and mechanical properties of the Al–C, Al–N and Al–C–N thin films deposited by the reactive r.f. magnetron sputtering was studied. The structure, chemical composition and bonding were examined by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and Fourier transformed infrared spectroscopy (FTIR), respectively. Finally, the mechanical properties were determined by nanoindentation.

2. Experimental setup

Al–C, Al–N and Al–C–N films were grown onto Si [100] substrates by r.f. reactive magnetron sputtering (13.56 MHz). Al–N coatings were obtained by sputtering of Al (99.9%) target in Ar/N$_2$ (4/1) atmosphere.

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Al–C and Al–C–N were obtained by co-sputtering of a binary (50% Al, 50% C) target in argon and in Ar/N$_2$ (4/1) mixture, respectively. During the deposition process the d.c. bias voltage was varied fixing the other deposition parameters, in order to investigate its influence on the mechanical properties of deposited films. The deposition chamber was evacuated at 10^{-5} mbar before the films growth process by means of a turbomolecular pump. The working pressure was 6×10^{-3} mbar and the r.f. power applied to the target and deposition temperature were 100 W and 400 °C, respectively.

The films were characterized by X-ray diffraction (XRD) using a Rigaku DMAX 2100 difractometer with a Cu Kα (λ = 1.5418 Å) radiation source. Elemental composition of the films was measured by energy dispersive X-ray spectroscopy (EDS) by means of a Hitachi-2500 microscope equipped with a window to the detection of light elements. The Fourier transform infrared analysis of the films were made with a Shimatzu 8000 (350–4600 cm^{-1}) spectrometer, that uses a ceramic type Nernst source. The thickness of the films was obtained by means of profilometry. The mechanical analyses were performed by nanoindentations using at variable load a Ubi1-Hysitron device and a diamond Berkovich tip. The results were evaluated by the Oliver and Pharr method [14] and the curves of hardness as a function of penetration depth were fitted by the Korsunsky's model [15].

3. Results and discussion

3.1. XRD results

XRD analysis for the Al–C, Al–N and Al–C–N films deposited at different bias voltages showed that these are amorphous and no reflections from the deposits can be detected in the patterns, in contrast with almost results reported elsewhere [7,16–20] where defined peaks were associated to Al$_4$C$_3$ and w-AlN phases. Several authors observed that contaminated AlN films, particularly with oxygen, were also amorphous [21,22]. In this case, the contaminants inhibit the formation of the AlN wurtzite structure. Substrate bias had no considerable effect on phase constituents. Only peaks associated with the Si [100] substrate signal were recorded.

3.2. EDS analysis

EDS analysis of the prepared films is shown in Fig. 1a,b for the Al–N and Al–C–N, respectively. The applied d.c. bias has an obvious effect in the atomic composition of the samples. For all the Al–C, Al–N and Al–C–N films, as the bias polarization voltage is increased the aluminum content has a tendency to diminish.

The decreasing of Al atoms from the target to substrate as a function of the polarization voltage can be due to the re-sputtering process caused by the ionic bombardment. For Al–N films (Fig. 1a), an increase in the bias voltage leads directly to an increase of the nitrogen content in the films. This behavior can be attributed to a competition of mechanisms that involve nitrogen incorporation into the films, and at higher d.c. bias a selectively chemical sputtering acts on the aluminum atoms. Moreover, for Al–C–N films (Fig. 1b) the nitrogen content shows no variation with the applied bias voltage, probably because 21 at.% of N is a saturation content. It is worth noting that similar trends have been reported using different deposition systems [23,24]. On the other hand, in the Al–C films the carbon content (52–57%) is larger that in Al–C–N films (35–38%), because Al–C coatings were obtained by co-sputtering of a binary (50% Al, 50% C) target in pure argon and in Ar/N$_2$ (4/1) mixture for Al–C–N films. For this reason, during the deposition process of Al–C–N films, the quantity of sputtered carbon atoms from the binary Al–C target is lower than in pure argon. All films presented oxygen contamination (~5%), due to the presence of residual oxygen in the deposition chamber associated to the working pressure for coating deposition (6×10^{-3} mbar).
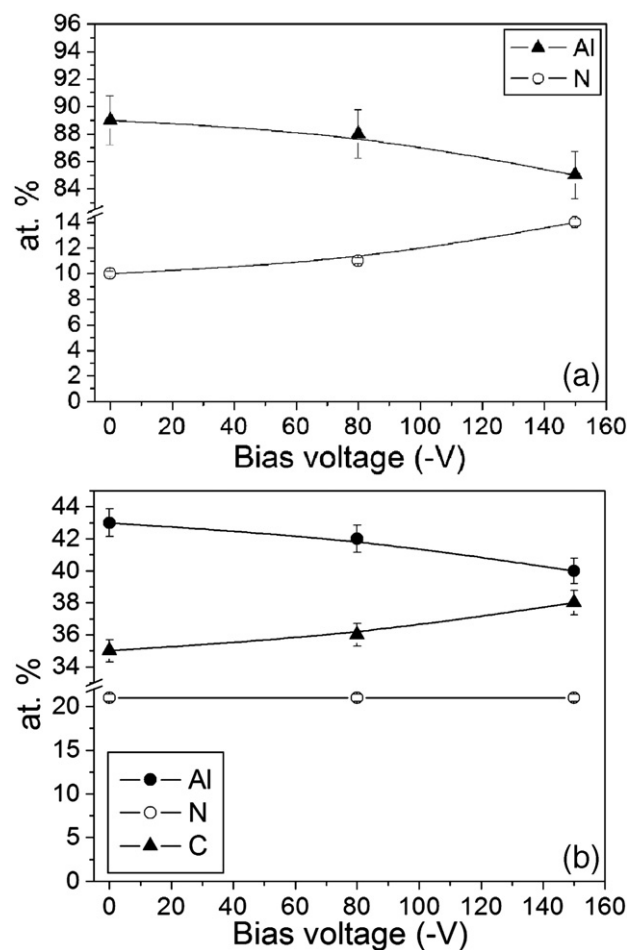

Fig. 1. Atomic percentage of a) Al–N and b) Al–C–N films, as function of bias voltage.

3.3. FTIR analysis

FTIR spectra of Al–C, Al–N and Al–C–N films grown without bias voltage are shown in Fig. 2a,b,c. For the Al–C film, the presence of active modes associated to stretching Al–C bonds at 770 cm^{-1}, other modes around 550 and 660 cm^{-1} which can be ascribed to Al–O stretching mode and O–Al–O bending mode, respectively, and a wide band related to C–C and C=C bonds between 1350 and 1700 cm^{-1} are observed [25,26]. In general, the FTIR spectra of the Al–C films show a small increase of the peak area related to the Al–C bonds, when the bias voltage increases.

From Fig. 2b, the presence of an active mode at 680 cm^{-1} associated to the *wurtzite* phase of the Al–N, [25], and at 540 cm^{-1} associated to Al–O stretching mode, respectively [26,27] are shown. In this case, when the bias voltage is upward the peak area associated to the *wurtzite* phase fitted with a Gaussian function is increased, probably related to the increase of nitrogen content as showed in EDS analysis. As mentioned before, the *wurtzite* phase was not observed in the XRD patterns, which can be due to a short range ordering of this. The amorphous character of the Al–N films is confirmed here as a wide band.

Finally, Fig. 2c shows the presence of active modes related to the *wurtize* Al–N and Al–C bonds around 680 and 770 cm^{-1}, respectively, and at 550 cm^{-1} to stretching Al–O bonds in aluminum oxides. A wide band between 1350 and 1700 cm^{-1}, related to C–C, C–N, C=C and C=N bonds, and other band at 2200 cm^{-1} associated to C≡N triple bonds, is also observed [25–27]. The effect of increase the bias voltage is the decreasing of the peak area associated to the *wurtzite* Al–N phase, while the area associated to stretching Al–C bonds remains almost constant.