Available online at www.sciencedirect.com

Diamond & Related Materials 14 (2005) 1348 – 1352

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Synthesis and characterization of superhard aluminum carbonitride thin films

A.L. Ji, L.B. Ma, C. Liu, C.R. Li, Z.X. Cao*

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, P.O. Box 603, Beijing 100080, China

Received 18 June 2004; received in revised form 11 January 2005; accepted 15 January 2005

Abstract

Oxygen-free aluminum carbonitride thin films were grown on Si (100) substrates by reactive magnetron sputtering of Al target with the gas mixture of Ar, CH_4 and N_2 as precursor. A complementary set of techniques including X-ray photoelectron spectroscopy, energy-dispersive X-ray spectrometry, X-ray diffraction, transmission electron microscopy and atomic force microscopy was employed for the characterization of the deposit chemistry, structure as well as morphology. Film growth proceeds along the preferred [0001] direction with the basal planes twisted because of the frustration in arranging the building blocks for aluminum carbonitrides. Under given conditions, the deposits show a declining tendency of crystallization with increasing carbon content. Strong covalent bonding and structural disorder give the film's extreme mechanical rigidity: Berkovich hardness is over 27.0 GPa for all the deposits, and an extreme value of 53.4 GPa was measured in $Al_{47}C_{20}N_{33}$.

Keywords: Aluminum carbonitride; Magnetron sputtering; Thin film; Hardness

1. Introduction

Covalent compounds comprising light elements have many excellent properties such as wide band gap, superior chemical and mechanical stability, due to the small atomic radius and strong interatomic bonding. Among them, carbides, nitrides and borides of silicon and aluminum have attracted considerable interest from multidisciplinary researchers and have found extensive applications in various industry branches besides microelectronics and optoelectronics [1–3]. In recent years, the research work has been shifting gradually, but steadily, from the binary materials to ternary ones, since there is a much larger space of property tuning in the latter. Generally, the atomic and/or electronic structures of a ternary system can be tailored by composition modification, for instance, to obtain a particular quality. Various deposition techniques have been exploited in the synthesis of ternary compounds of light elements such as B–C–N and Si–C–N, and a wealth of excellent materials properties have been manifested in such systems [4–8].

It can be anticipated that the ternary Al–C–N compounds will show some individual characteristics as they contain metal atoms. In fact, the complementary combination of properties such as extreme electrical insulation, high dielectric constant, readiness of metallization and so on promises multifaceted applications of aluminum carbonitrides in electronics. The ternary Al–C–N system provides a host of wide-gap materials as illustrated in Fig. 1, yet more novel structures are waiting to be thoroughly explored. Recently, there is an increasing effort targeted at Al–C–N and also quaternary compounds containing these three elements—novel structures and high-quality thin films [9]. In 2001, Kouvetakis's group first succeeded in synthesizing the cyanide crystal $Al(CN)_3$ using a wet chemistry method [10]. According to our first principles calculation, this new aluminum carbonitride has a direct band gap of about 7.0 eV, as calibrated against the wurtzite AlN. Jiang et al. prepared the Al–C–N thin films with reactive sputtering in

---

* Corresponding author.

E-mail address: zxcao@aphy.iphy.ac.cn (Z.X. Cao).

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2005.01.036

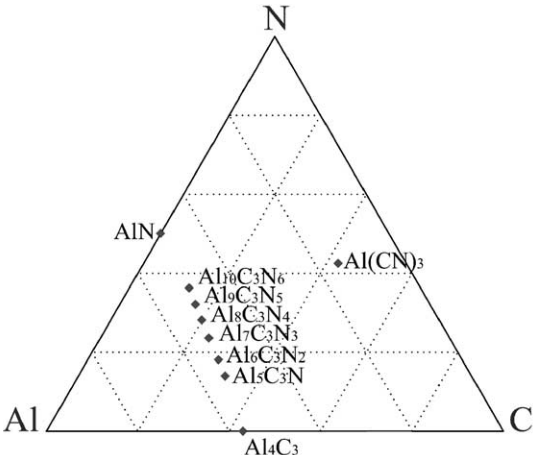

Fig. 1. Ternary Al–C–N composition triangle showing the currently available stoichiometric compounds.

the hope that the incorporation of aluminum may stabilize the hypothetical β-C_3N_4 structure [11,12]. In the present work, we report the synthesis of oxygen-free, polycrystalline aluminum carbonitride films with reactive magnetron sputtering. A complementary set of techniques has been employed for the chemical and structural characterization of the deposits. Nanoindentation reveals a maximum hardness nearly at the lower limit for natural diamond.

2. Experimental

Films were grown on Si (100) substrates by reactive magnetron sputtering of aluminum target (4 N purity) with the gas mixture of argon, nitrogen and methane. Before being transferred into the preparation chamber of a custom-designed magnetron film growth facility, which was pre-evacuated to a pressure ~10^{-4} Pa, the substrates had been ultrasonically cleaned successively in alcohol and acetone and rinsed with de-ionized water following 3-min etching in 1.0% HF solution to remove the native oxide. As a matter of routine, the target would be presputtered under proposed growth conditions for 1 h in order to obtain a required metal-atom supply. In the course of film growth, the substrate temperature was held at 300 °C, the pressure maintained at 1.6 Pa, and the total gas flow rate kept at 4.0 sccm, of which 2.4 sccm reserved for argon. Composition regulation for the deposits was realized through varying the flow rates of nitrogen and methane—for the ternary deposits concerned here, the flow ratio $CH_4/(CH_4+N_2)$ was varied from 5% to 25% at a 5% interval.

The chemical composition of the deposits was determined by energy-dispersive X-ray spectrometry (EDX) attached to a scanning electron microscope (Sirion, Fei) excited with a primary electron energy of 10 KeV, together with X-ray photoelectron spectroscopy (ESCA-lab) using the Mg Kα line ($h\nu$=1253.6 eV), which was also exploited to study the bonding states. Transmission electron microscopy (TEM, Tecnai F20) and X-ray diffraction (XRD, Rigaku, D/max-2500 PC) using the Cu Kα irradiation were employed for structural characterization. Surface morphology of the films was assessed by an atomic force microscope (AFM, Digital Instruments) operated in contact mode. In doing the hardness measurement with a Berkovich indenter (CSEM), the maximum load was carefully manipulated to restrict the indent depth within 80 nm, so that the influence of the soft substrate is negligible.

3. Results and discussion

Under given conditions, films of a thickness varying about 1.3 μm, as determined from the cross-sectional scanning electron micrographs, were obtained after a 2-h growth. Oxygen-free aluminum carbonitride films were obtained, as confirmed by the EDX spectrum shown in Fig. 2. For the comparison study presented in this work, the samples are AlN, $Al_{49}C_{13}N_{38}$, $Al_{50}C_{15}N_{35}$, $Al_{47}C_{20}N_{33}$, $Al_{48}C_{25}N_{27}$ and Al_4C_3, for which the composition was calculated from both the XPS and EDX spectral data. It is noteworthy that, under given conditions, the content of Al in the resulting aluminum carbonitride films remains at about 50%, while that of C and N competes. To infer the chemical binding in the deposits from XPS spectral lines, we make a close examination of the sample $Al_{47}C_{20}N_{33}$ as an example. In Fig. 3, the Al 2p line centered at 74.1 eV has a well-developed, featureless spectral profile; the full-width-at-half-maximum is 1.97 eV, which is a typical value for Al in AlN and sapphire [13]. The C 1s line is much broader than the N 1s line. It can be decomposed into three distinct peaks with a center separation of 4.0 eV; for the N 1s line this is however less than 2.5 eV. Moreover, the main peak in C 1s line also has a lower weight in the whole profile than in the case of N 1s line. Considering as well the fact that only one Raman spectral line at about 660 cm^{-1}, corresponding to the Al–N E_2^2 mode [14], is detectable (not shown) in the

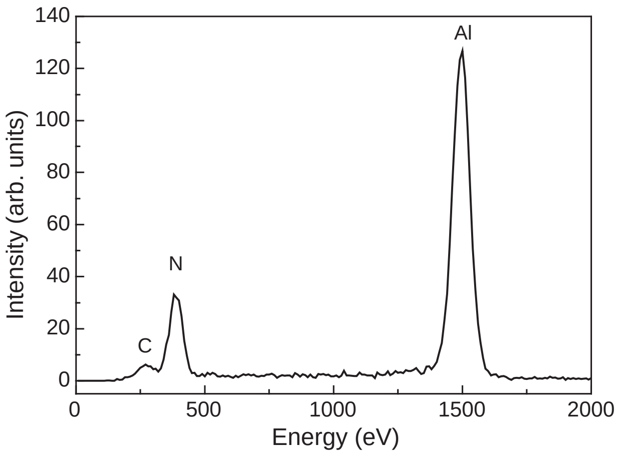

Fig. 2. Typical EDX spectrum for the aluminum carbonitride deposit. No trace of oxygen contamination can be recognized.