Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 4738–4744
www.elsevier.com/locate/tsf

Effect of pressure and substrate temperature on the deposition of nano-structured silicon–carbon–nitride superhard coatings by magnetron sputtering

S.K. Mishra *, Chander Shekhar, P.K.P. Rupa, L.C. Pathak

National Metallurgical Laboratory, Jamshedpur, 831007, India

Received 18 July 2005; received in revised form 14 February 2006; accepted 28 November 2006
Available online 24 January 2007

Abstract

A systematic investigation on the deposition of silicon–carbon–nitride (Si–C–N) films under varying deposition conditions such as pressure, substrate temperature and nitrogen content was carried out by radio frequency and direct current magnetron sputtering techniques. Significant role of the different deposition parameters on hardness and structure in the film was observed. It was observed that there was a certain range of nitrogen to argon partial pressure ratio (90:10 to 98:2) for which the particle size was reduced and the films were smooth with fine particle growth, beyond this limit the films had larger particle growth and roughness. The hardness of the deposited film varied between 4400 Hv and 473 Hv depending on deposition condition. Si–C–N film with hardness above 4400 Hv by reactive RF magnetron sputtering from SiC–C composite target in nitrogen–argon was obtained. X-ray diffraction studies revealed the amorphous nature of the deposited films, whereas nano-crystallinity of the particles was noticed during atomic forced microscopy observations. X-ray photoelectron spectroscopy analysis showed the presence of C–N and Si–N bonds in the harder films. It was found that the presence of β-C_3N_4, Si_3N_4 and graphite phases and the particle growth in the deposited films control the hardness of the film.

Keywords: Atomic forced microscopy; Hardness; Silicon carbon nitride; Sputtering

1. Introduction

Recently, the ternary silicon–carbon–nitride (Si–C–N) system has drawn immense interest due to its excellent and exciting new properties in comparison to the crystalline Si_3N_4 and SiC duel phase counterpart. It has high resistances to oxidation and wear, excellent chemical stability, wide band gap and promising mechanical and thermal properties, ideal for applications as wear and oxidation resistant, and as optoelectronic material in hostile environment [1,2]. The Si–C–N system is expected to have different superhard phases namely SiC, β-Si_3N_4 and β-C_3N_4 phases, which is a superhard material with theoretically predicted hardness near to diamond [3]. The β-C_3N_4 and β-Si_3N_4 having similar crystal structures are expected to be miscible in each other and form Si–C–N phase with excellent hardness. All these have rapidly increased the research activities on synthesis of Si–C–N compounds and several methods for the fabrication of amorphous and crystalline Si–C–N films are reported in literature [4–10]. Amongst them, microwave plasma chemical vapour deposition [4,5], plasma enhanced chemical vapour deposition [6,7], ion beam implantation [8], and magnetron sputtering [9,10] are significant and have been used for the deposition of Si–C–N film.

Magnetron sputtering is one of the most versatile techniques to deposit good quality films at low temperatures and the process is easy to scale up. In this paper, we report the effect of deposition pressure and substrate temperature on the hardness, structure of Si–C–N thin film deposited by radio frequency (RF) and direct current (DC) magnetron sputtering techniques. X-ray photoelectron spectroscopy (XPS) analysis of few films and its correlation with the properties are also discussed.

* Corresponding author.
E-mail address: suman@nmlindia.org (S.K. Mishra).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.11.167

2. Experimental details

A graphite disc having a diameter of 5 cm and 3 mm thick was covered with 1.0 mm thick layer of silicon powder and subsequently heated at 1800 °C under argon atmosphere in a graphite resistance furnace (Astro, Thermal Technology Inc. USA). Good shining SiC–C composite target was prepared by a reactive infusion technique of silicon into graphite matrix. The deposition chamber was pumped down to $\sim 8\times10^{-4}$ Pa and after that the substrate heater capable of heating the substrates to a maximum of 900 °C was switched on. The films were deposited by either RF or DC magnetron sputtering techniques at different deposition conditions using a balanced magnetron sputtering system (HINDHIVAC Pvt. Ltd, India). Initially the chamber pressure was adjusted to 1×10^{-1} Pa by introducing only argon gas into the deposition chamber. Subsequently nitrogen was introduced into the vacuum chamber to maintain different deposition pressures of 4×10^{-1} Pa, 1.0 Pa, 5.0 Pa, and 10.0 Pa. From the partial pressures of the constituent gases inside the deposition chamber, the partial pressure ratio of N_2 to Ar has been calculated to be 75:25, 90:10, 98:2 and 99:1 at the above pressures respectively. A RF power of 400 W with maximum reflected power of 10% was used to deposit the Si–C–N films by RF magnetron sputtering technique, whereas, in the case of DC magnetron sputtering, the films were deposited at 120 W DC power. The substrates were kept at room temperature (~30 °C), 300 °C, 500 °C and 700 °C during deposition. Few films were also deposited in only nitrogen plasma, at 1 Pa both at room temperature and 500 °C substrate temperature using DC power. All the depositions were carried out on ultrasonically cleaned (in acetone medium, dried and immediately put into vacuum chamber) Si substrate. The X-ray diffraction (XRD) analyses of the deposited films were carried out with Co Kα source using Schiefert X-ray diffractometer, Germany.

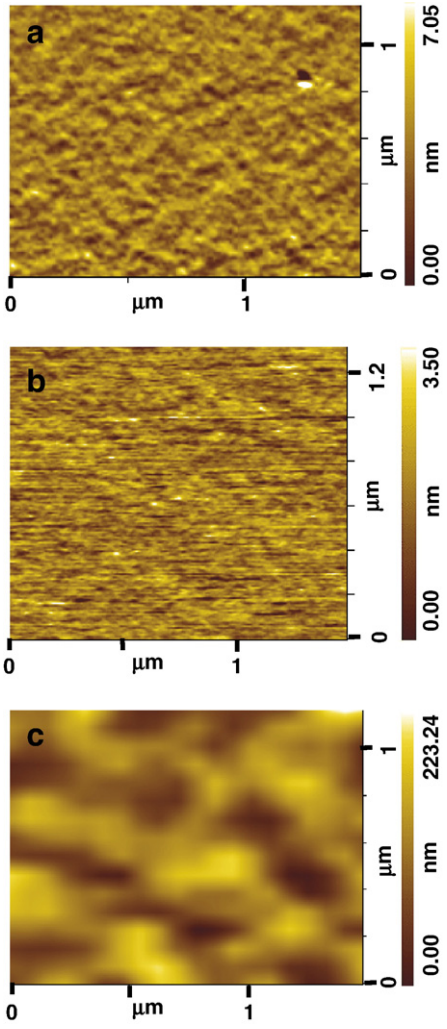

Fig. 1. AFM topography images of Si–C–N films deposited at 500 °C substrate temperature by RF magnetron sputtering in Ar/N_2 plasma at different deposition pressures: a) 4×10^{-1} Pa, b) 1.0 Pa and c) 10 Pa. *Z*-axis scale is given in the right side of the figure.

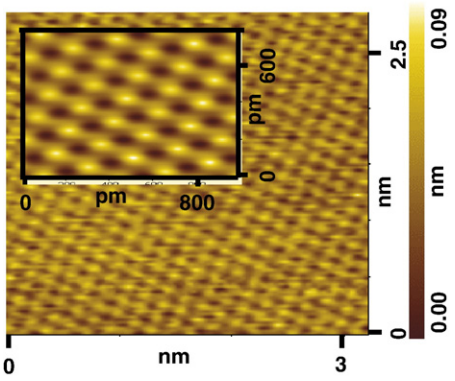

Fig. 2. High-resolution AFM topography (unfiltered) image for the films deposited by 400 W RF magnetron sputtering at 4.0×10^{-1} Pa on Si substrate at 500 °C in Ar/N_2 plasma showing the atomic arrangements resembling a lattice. The atomic arrangements are shown in the inset. *Z*-axis scale is given in the right side of the figure.

The atomic force microscope (Seiko Scanning Probe Analyzer 400, Japan) was used to study the surface topography and microstructure of the deposited films. For the contact mode atomic forced microscopy (AFM) investigation, we have used a 20 µm piezo scanner, a sharp gold-coated Si_3N_4 tip, and a scan rate of 4.8 to 5.75 Hz. Different locations on the coatings were investigated in random position. After capturing, the images were flattened using line by line leveling method and a two-dimensional fast Fourier transform (FFT) was performed to produce a reciprocal space representation, on which spots were selected for reverse transformation to generate the amplitude of each periodicity in various parts of the high-resolution AFM image. The average particle sizes, roughness values of the deposited films and the interplanner spacings (from the line profile on the atomic resolution pictures) were calculated using image processing software.

Leica microhardness unit (VMHT Auto, Germany) was used to measure the hardness values of the films by applying a load of 15 g. The average values obtained from 15 indents on the films are reported as hardness value. The XPS analysis of the deposited Si–C–N films was carried out with incident Mg–Kα radiation having kinetic energy of 1253.6 eV. The spectra were recorded at pass energies of 50 eV and for each element the