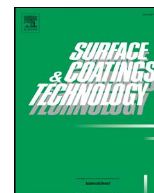
Surface & Coatings Technology 334 (2018) 536–542

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat



Investigation of composition of boron carbide thin films by resonant soft x-ray reflectivity

P.N. Rao[a,b,*], R.K. Gupta[a], K. Saravanan[c], A. Bose[d], S.C. Joshi[d], T. Ganguli[a,b], S.K. Rai[a,b]

[a] Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India
[b] Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400 094, India
[c] Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamilnadu, India
[d] Proton Linac and Superconducting Cavities Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, India

ARTICLE INFO

Keywords:
Boron carbide
Optical index
Composition
Protecting layer
X-ray multilayers
Resonant reflectivity

ABSTRACT

Boron carbide thin films of different thicknesses deposited by ion beam sputtering were studied. The deposited films were characterized by grazing incidence hard x-ray reflectivity (GIXR), resonant soft x-ray reflectivity (RSXR), x-ray photo electron spectroscopy (XPS), resonant Rutherford backscattering spectrometry (RRBS), and time of flight secondary ion mass spectrometry (TOF-SIMS). Depth profile of the chemical elements constitute the films is reconstructed based on analysis of reflectivity curves measured in the vicinity of B K-edge. The composition of films is closely dependent on film thickness. Boron to Carbon (B/C) ratio reaches to ~4 as the thickness of deposited films increases. The B/C ratio estimated from RSXR measurements are in agreement with the RRBS measurements. TOF-SIMS data also suggested that decrease in boron content with decrease in film thickness. XPS measurements confirm the presence of little amount of B atoms on the surface of low thickness film.

1. Introduction

Boron carbide is an important x-ray optical element in both hard and soft x-ray regions [1–4]. It is also an important barrier material to minimize the inter diffusion in multilayers (MLs) [5]. Boron carbide which has a very high melting and sublimation point is one of the suitable candidates for free electron laser applications [6–8]. It is used as capping layer on top of the ML structure to protect ML structure from oxidation [9]. Boron carbide is also a promising material for the next generation photo lithography applications at 6.x nm (the value of x still has to be determined by industry) wavelength [10,11]. The compositional changes in the boron carbide causes significant changes in its optical constants in the vicinity of B K-edge and limits maximum achievable throughput from boron carbide based MLs [12]. The optical band gap of boron carbide and the properties of boron carbide/Si diodes can be varied by simply changing composition of boron carbide [13–15]. In many practical applications boron carbide thin films with thickness ranging from a fraction of a nanometer to several nanometers have been used. It is thus important to study the thickness dependent compositional changes in boron carbide thin films.

In our previous work [12,16] on C/B_4C MLs, we observed deviation in derived optical constants of boron carbide from the values available in literature [17]. A detailed analysis in Ref. 12, suggested that the boron deficient/carbon rich growth in boron carbide layer. In that work we concluded that presence of excess carbon in the boron carbide layer is either due to inter-diffusion of C atoms from the C layer or due to change in stoichiometry of deposited boron carbide layer from the target (B_4C) stoichiometry. To investigate further the compositional changes in boron carbide we have chosen thin films of boron carbide in this study. In general ion and electron beam techniques are used to determine concentration profiles of thin films. Electron beam techniques like X-ray photo electron spectroscopy and Auger electron spectroscopy are surface sensitive and depth information is obtained by etching out the material. These techniques are destructive in nature and consequently repetitive measurements on specimen cannot be possible [18]. Grazing incidence hard x-ray reflectivity (GIXR) is routinely used technique to derive layer thicknesses, surface and interface roughness of thin films and MLs. However, the availability of synchrotron sources with high brilliance and tunable energy provide the opportunity for researchers to explore additional properties apart from structure using reflectivity technique. In the vicinity of the absorption edges optical index is strongly depends on the composition of layers. The reflectivity measured in the vicinity of absorption edges has opened up possibility to derive composition of thin films in nondestructive way. The angular

* Corresponding author at: Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India.
E-mail address: pnrao@rrcat.gov.in (P.N. Rao).

https://doi.org/10.1016/j.surfcoat.2017.12.010
Received 4 August 2017; Received in revised form 2 December 2017; Accepted 4 December 2017
Available online 05 December 2017
0257-8972/ © 2017 Elsevier B.V. All rights reserved.

dependence inherent to reflectivity measurements provides the depth resolution down to nm with penetration depths over hundreds of nanometers. Resonant soft x-ray reflectivity (RSXR) has been used for characterization in low contrast organic thin films [19] and compositional analysis in thin film [20] and periodic multilayers [12].

In this paper we investigate the compositional changes in boron carbide thin films as a function of its thickness by combining GIXR and RSXR. X-ray photo electron spectroscopy (XPS), resonance Rutherford backscattering spectrometry (RRBS) and time of flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed to complement the observation made from RSXR.

2. Theoretical background

In the x-ray region, response of the medium is described by energy dependent complex refractive index $n = 1 - \delta + i\beta$, where δ (dispersion coefficient) and β (absorption coefficient) are the optical constants [1]. The reflection or refraction at a boundary between two media occurs due to change in refractive index. Specular x-ray reflectivity is one of many x-ray scattering techniques used to probe the profile of film along the direction perpendicular to the sample surface. When probing thin films with reflectivity, one generally characterizes the interference of rays reflected from different interfaces as a function of momentum transfer vector q, defined as $q = q_{in} - q_{out} = 4\pi \sin\theta/\lambda$, where q_{in} and q_{out} are incident and reflected momentum transfer vectors respectively,θ is the grazing incidence angle and λ is the wavelength of probing beam. The modulations in reflectivity profile measured using shorter wavelengths were analyzed to get the geometrical parameters like thickness and root mean square (rms) interface and surface roughness. In case a film contains low-Z elements, the difference in electron density among low-Z elements is small, thereby limiting the observable contrast in conventional GIXR. We thus can get limited information on the depth distribution of film contains low-Z elements using GIXR.

In the vicinity of the absorption edge both the optical constants δ and β undergo strong variations. For many light elements absorption edge falls in the extreme ultraviolet/soft x-ray region. Any small changes in the composition of film gives rise to a significant change in optical index contrast and that can give a clear contrast in a reflectivity profile. Thus analysis of the reflectivity curves measured near the absorption edges gives the concentration profile of all elements in the sample. The angular dependence inherent to reflectivity measurements brings furthermore the spatial selectivity. If a sample contains several chemical elements the optical indices can be represented as

$$\delta = 2.7007 \times 10^{-4}\lambda^2\rho\frac{\sum_j X_j (f^0_{NR,j} + f'_{R,j}(\lambda))}{\sum_j X_j\mu_j} \tag{1}$$

$$\beta = 2.7007 \times 10^{-4}\lambda^2\rho\frac{\sum_j X_j f''_{R,j}(\lambda)}{\sum_j X_j\mu_j} \tag{2}$$

where λ is the incident wavelength [nm], ρ is the density [g/cm^3], X_j is the atomic fraction of j atoms, and μ_j is the atomic weight of j atoms [g/mol], $f_{NR}{}^o(q)$ is the non-resonant atomic scattering factor (ASF), $f_R{}'(\lambda)$ and $f_R{}''(\lambda)$ are respectively the dispersion and absorption corrections to the ASF arise from the bounded electrons in an atom. In the present study we deduce the concentration profiles of all chemical elements present in the film from the optical index derived from the reflectivity curves measured in the vicinity of B K-edge. In order to take into account the effects of bonding between B and C in B_4C on the ASFs, we used ASFs for B derived from magnetron sputter deposited boron carbide thin films [17]. ASFs for non-resonating atoms like C and O were taken from the Henke et al. [21] tabulated values. The mass density obtained from GIXR measurements were used and best fits to the derived optical constants was obtained by varying the atomic fraction of different chemical elements in the film.

3. Experimental techniques

3.1. Sample preparation

Boron carbide thin films of various thicknesses were deposited on ultrasonically cleaned Si (100) wafer using ion beam sputtering technique. We used commercially available four inch sputtering target of 99.5% purity for B_4C. The base pressure of the system was $\sim 3 \times 10^{-5}$ Pa. During the deposition the Ar gas flow was fixed at 3 standard cubic centimeters which results in a vacuum drop to 6×10^{-2} Pa in the chamber. Ar ion-beam of current about 25 mA and voltage 1000 V was used to sputter the target material. Target material was pre sputtered for 30 min before the deposition of films. In the present study we used boron carbide films of thickness, (d) is in the range of 10–80 nm. The samples were named as S1 (d ~ 10 nm), S2 (d ~ 19 nm), S3 (d ~ 30 nm), S4 (d ~ 40 nm), and S5 (d ~ 80 nm).

3.2. Reflectivity measurements

GIXR measurements were carried out [Bruker discover D8 diffractometer] using Cu K_α radiation ($\lambda = 0.154$ nm). The angle dependent soft x-ray reflectance measurements in the vicinity of B K-edge were carried out using the reflectivity beamline at Indus-1 synchrotron facility. This beamline, having a toroidal grating monochromator, delivers photons in the range of 4–100 nm, with high flux ($\sim 10^{11}$ photons/s), and has a moderate spectral resolving power ($\lambda/\Delta\lambda$) of 200–500. Various absorption edge filters are provided in the beamline to suppress the higher order contamination from the monochromator. A nonlinear least square curve fitting technique based on χ^2 minimization method was applied for the determination of microstructural parameters and optical constants from reflectivity curves [22].

3.3. Resonance Rutherford backscattering spectrometry (RRBS)

In general Rutherford backscattering spectrometry (RBS) is used for analysis of heavier elements on lighter substrate. However RBS is ineffective for detection of lighter elements on heavier substrate due to small scattering cross-section and overlap of background signal coming from heavier substrate. Resonant Rutherford backscattering spectrometry (RRBS) has been widely used for analysis of light elements on heavier substrate. In order to quantification of the elements oxygen, boron and carbon presents in the sample S4, RRBS measurements have been performed. The RRBS measurements were performed using 3.045 MeV He^{++} particles for the quantification of oxygen, 3.9 MeV He^{++} particles for the quantification of boron and 4.27 MeV He^{++} particles for the quantification of carbon as alpha particles has enhanced scattering cross-section with these elements at these energies. The 1.7 MV Tandetron accelerator (HVEE, The Netherlands) available at IGCAR, Kalpakkam was used for the RRBS analysis. The backscattered particles were detected using a Si surface barrier detector kept at an angle of 165° with respect to the incident beam direction. The concentrations of oxygen, boron and carbon in the samples were obtained from the best-fit of RRBS data using the SIMNRA program [23].

3.4. X-ray photo electron spectrometry (XPS)

XPS measurements were carried out using photoelectron spectrometer at a base pressure better than 5×10^{-10} mbar. Al K_α radiation ($\lambda = 8.34$ nm) was employed for recording the spectra with the source operated at an emission current of ~ 10 mA and an anode voltage of ~ 10 kV. XPS spectra were taken on the samples after sputter cleaning sample surface with Ar ions. Sputter cleaning of sample surface was

Download English Version:

https://daneshyari.com/en/article/8024707

Download Persian Version:

https://daneshyari.com/article/8024707

Daneshyari.com