Surface & Coatings Technology 272 (2015) 409–414

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Study of structural and optical properties of zirconium carbide (ZrC) thin-films deposited by ion beam sputtering for soft x-ray optical applications

Amol Singh *, Mohammed H. Modi, A.K. Sinha, Rajnish Dhawan, G.S. Lodha

Indus Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore 452 013 India

ARTICLE INFO

Article history:
Received 12 September 2014
Accepted in revised form 24 March 2015
Available online 1 April 2015

Keywords:
Soft x-ray reflectivity
Thin films
X-ray optics
Multilayers
X-ray reflectivity

ABSTRACT

Compound materials have shown stable and enhanced optical performance in soft x-ray energy region. However, the growth related change in structural and chemical properties lead to affect their performances. In the present study, thin films of different thicknesses of ZrC compound material were deposited on Si (100) substrate. Optical response of ZrC thin film was measured in soft x-ray energy region using Indus-1 reflectivity beamline. It was found that the soft x-ray reflectivity data of ZrC thin films cannot be explained with Henke's tabulated data. To understand this disagreement a detailed structural and chemical investigation was carried out using x-ray reflectivity, grazing incidence x-ray diffraction, atomic force microscopy and x-ray photoelectron spectroscopy techniques. It was found that the presence of unreacted carbon along with small oxygen in ZrC matrix is responsible for variation in optical constant value. Details of the investigations are discussed.

1. Introduction

Multilayers of ultrathin films comprised of low Z/high Z elements are largely used in a variety of applications in the soft x-ray energy region. Such multilayer poses a severe drawback of high chemical reactivity among the constituent elements. In Si based multilayers (e.g. Mo/Si, W/Si, Nb/Si, etc.), silicide formation is a common problem, when they are used at elevated temperatures in high heat load environment. To overcome this difficulty a barrier layer (of carbon, B_4C, etc.) is deposited in between low Z and high Z materials. Earlier, a barrier layer of B_4C was used between Mo and Si to prevent the chemical intermixing. However, inserting an extra layer leads to a phase variation in the waves reflecting from different interfaces at the Bragg condition and thereby resultant phase mismatch reduces the reflectivity performance. Moreover, the barrier layer should be ultra-thin in order to minimize the phase mismatch which requires a stringent deposition control. In literature, many reports are available where compound materials are used in multilayers. Recently, NbC/Si multilayer is proposed for extreme ultraviolet (EUV) applications [1], where NbC (metal carbide) layers are found non-stoichiometric [2, 3] and has significant amount of unreacted carbon. The presence of unreacted carbon in the near vicinity of metal species (Nb, Mo, Zr, etc.) may act as a barrier layer for the Si or other elements to prevent the chemical intermixing. The NbC/Si multilayer is found thermally stable up to 700 °C, without significant loss in reflectivity performance. A. F. Jankowski et al. have reported W/B_4C a better combination in comparison with W/C multilayers [4]. Near Al L-edge Qi Zhong et al. have reported Zr/Al multilayer for EUV applications. This Zr/Al combination is thermally unstable above 200 °C [5, 6] and later intermixing and formation of Al-Zr alloy is reported (above 200 °C). To improve the thermal stability, Zr may be replaced by a suitable compound material based on their optical constant contrast with Al. In Fig. 1 optical constants of Zr, ZrC and Al are plotted in 140–240 Å wavelength region. It is clear that the optical constant contrast between ZrC and Al is better than the contrast between Zr and Al.

The reflectivity performance of a material depends on several growth related parameters. When thin films of compound material are formed from bulk target, their structural properties get modified because of change in near neighbour environment and confinement effects. If the chemical stoichiometry varies, the optical properties get modified [7] which leads to affect the optical performances. Hence the suitable compound materials must be investigated thoroughly for their structural and optical performances by pursuing a detail scientific study prior to their use in actual applications. Deposition of high quality ZrC thin films are difficult due to its high melting point, low evaporation and sputtering rate, high reactivity of Zr with oxygen and water vapours. Earlier several techniques are used for the deposition of ZrC thin films such as DC magnetron sputtering, e-beam evaporation, pulsed laser deposition (PLD), etc. In PLD technique a laser fluence around 10 J/cm^2 is required for deposition of ZrC films, which is difficult to be implemented [8]. Deposition of high quality ZrC films requires optimization of several deposition parameters to obtain high density and low surface roughness.

* Corresponding author.
E-mail addresses: amolphy@rrcat.gov.in, rrcat.amol@gmail.com (A. Singh).

http://dx.doi.org/10.1016/j.surfcoat.2015.03.033
0257-8972/

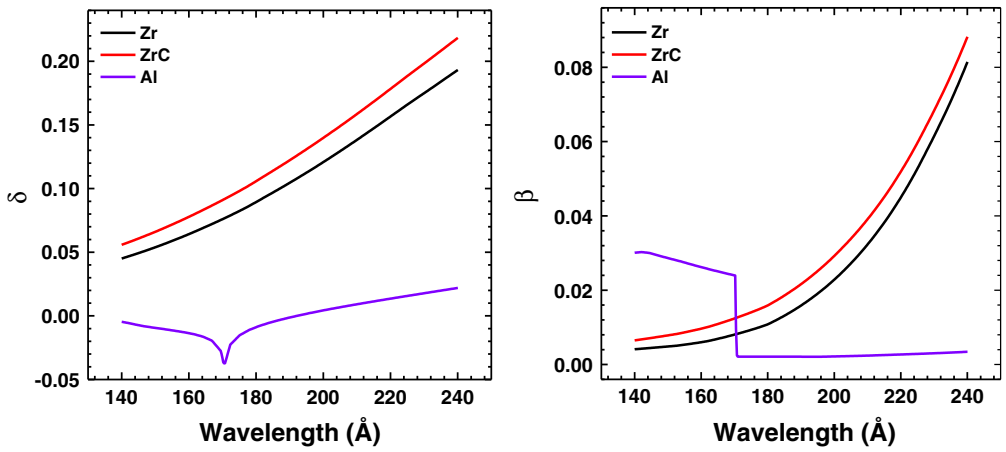

Fig. 1. Comparison of the optical constants of ZrC and Zr with Al in 140–240 Å wavelength region is shown near Al absorption edge. δ and β contrast for ZrC and Al is better suggesting it as a better choice over Zr.

In the present study we have grown ZrC thin films using ion-beam sputtering technique for detailed structural and optical characterizations. Structural and optical properties are studied using several experimental techniques such as soft x-ray reflectivity (SXR), x-ray reflectivity (XRR), grazing incidence x-ray diffraction (GIXRD), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) etc.

2. Experimental procedure

Thin films of ZrC of different thicknesses (100 Å, 200 Å and 300 Å) were deposited on Si (100) wafer using ion beam sputtering technique. Deposition was carried out under argon ambient at constant pressure of 6×10^{-2} Pa. Prior to that a base pressure of 3×10^{-5} Pa was achieved. A commercially available 4 in. sputtering target of ZrC (99.99% purity) was used. After process optimization, it was found that the films deposited at beam voltage of 1 kV and a gas flow rate of 3 standard cubic centimetres per minute are better in rms roughness.

SXR measurements were carried out using reflectivity beamline [9] at Indus-1 synchrotron radiation source. The reflectivity vs angle scan were performed in 0–65° incident angle using λ = 100 Å wavelength. Reflectivity vs wavelength scans were carried out at different incident angles. Optical constants of the materials available from CXRO database [10] were used for the data analysis.

XPS measurements were performed using an Omicron EA-125 photo electron spectrometer working at a base pressure of ~6.7×10^{-8} Pa. Al source operated at 10 kV anode voltage and 10 mA emission current was used for x-ray emission. XPS spectra were recorded after different sputtering cycle (as deposited, 10, 20, 30 and 50 min). A 4 kV, 1 μA/cm^2 Argon ion beam was used to sputter the sample. After each sputtering survey and core (C 1s, O 1s and Zr 3d) spectrum were recorded. XPS spectra were analysed and elemental concentration in depth of the film was obtained.

XRR measurements in hard x-ray region were performed using a BRUKER D-8 system consisting of θ–2θ goniometer and x-ray source of Cu target at λ = 1.54 Å Cu-Kα. All the measurements were performed with a step size of 0.005° in theta axes. Parratt formalism [11] was used to analyse reflectivity data. Effect of surface roughness was taken into account using Névot–Croce model [12]. A nonlinear least square refinement routine based on Genetic algorithm was used to refine fitting parameters [13].

GIXRD measurements of all samples were performed at angle dispersive x-ray diffraction (ADXRD) beamline [14] on Indus-2 synchrotron radiation source [15]. The beamline consists of a Si (111) double crystal monochromator and two experimental stations namely a six circle diffractometer with a scintillation point detector and Mar-.345.dtb Image plate area detector [16]. In the present study GIXRD measurements were carried out using the image plate detector. Incident monochromatic beam was fixed at an angle of 0.5° and GIXRD pattern was recorded using the image plate detector. The wavelength and the distance between the sample and detector were calibrated using XRD pattern of NIST standard LaB6 powder. GIXRD data was integrated using Fit2D software [17].

AFM measurements were carried out using the instrument Nanoscope III from Digital Instrument. AFM measurements were performed over 1 μm, 2 μm, 5 μm and 10 μm scale in close contact mode over 256 × 256 pixel area. AFM data measured over different length scales were combined together to generate a single power spectral density (PSD) over a large spatial frequency range. The rms roughness was determined by integrating the PSD in 10^{-1} to 10^{-4} nm^{-1} range [18].

3. Results and discussions

Soft x-ray reflectivity versus angle measurement of 300 Å thick ZrC thin film was carried out using λ = 100 Å incident wavelength. Measured and fitted SXR curves are shown in Fig. 2. In the inset of the Fig. 2, the optical density profile obtained from the fit parameters of SXR data is shown where a dotted horizontal line represents the bulk delta value of the ZrC material. The SXR data is fitted assuming a three layer model. The model comprised of a native oxide layer of ~30 Å on

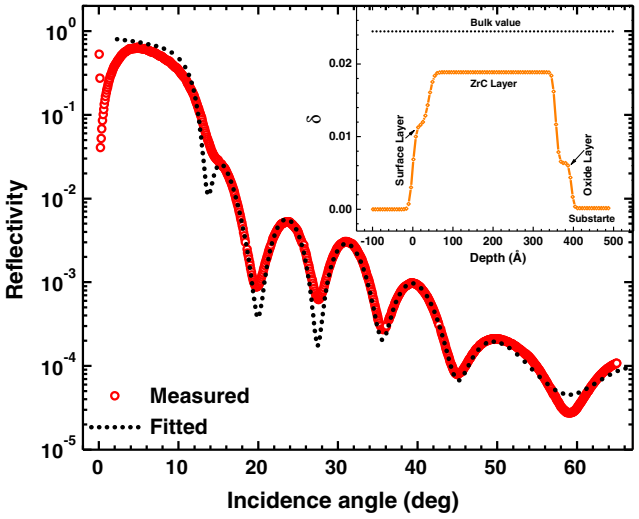

Fig. 2. Measured and fitted SXR data of 300 Å ZrC thin film for 100 Å wavelength. In the inset optical density profile obtained from the fit parameters is shown. For the reference, the bulk delta value is shown by black dotted line.