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Structures, morphologies, and chemical states of sputter-deposited CrZrN thin films with various Zr contents

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ABSTRACT

Chromium zirconium nitride (CrZrN) thin films were prepared on Si wafers and glasses at various Zr contents by reactive DC magnetron co-sputtering of Cr and Zr metals in Ar and N_2 mixture without voltage biasing and external heating. Influences of the Zr contents on crystal structure, cross-section morphology, surface morphology, and chemical composition and chemical state were investigated by X-ray diffraction, field emission scanning electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy, respectively. The results showed that N content in the films was increased when Zr content increased. Film microstructure changed from coarse columnar to finer-grain morphology and film surface became smooth caused by grain refinement. Zr–metal and Zr–N bonding fractions were increased with the increasing Zr content, whereas Cr–N was decreased due to being substituted by Zr of Cr atoms in the fcc B1 type crystal structure of (Cr, Zr)N. In addition to an increase in lattice parameter, the substitution of Zr could lead to an increase in interatomic distances which affected bonding length between metals and nitrogen atoms. According to the charge potential model, the increase in bonding distances between atoms resulted in negative shifts in binding energy of electrons of all elements that led to observation of lowering in the separation between photoelectron lines of Cr, Zr, and N elements. The lower separation with the increase of Zr content suggested that bonding between metals and nitrogen became stronger due to the dominance of the covalent character as evidenced by the enhanced hardness of the CrZrN materials.

1. Introduction

Ternary nitride thin films of the form A–B–N which A and B are metal elements have been invented with a goal for combining good properties of binary nitride materials such as TiN, CrN, ZrN, and AlN to solve the degradation of mechanical properties at a temperature above 500 °C and to improve film structures for protecting the substrate surface from an environment [1–7]. Due to the oxidation resistance at high temperature of CrN material, the ternary nitride films such as CrTiN [8, 9], CrAlN [10], CrWN [11], CrSiN [12], and CrZrN [13–16] have been extensively studied. Among these films, the CrZrN shows the superior properties with good promise as a protective coating for many applications. Kim et al. [14] reported enhancements of film hardness and elastic modulus with increasing Zr content. The surface of the film become very smooth and the coefficient of friction is dramatically decreased. In addition to mechanical properties, Aouadi et al. [15] studied optical and chemical properties of the film as a function of Cr content. Their results reveal similarity in optical behavior between CrZrN film and metallic materials. An increase in the Cr content leads to rising in density of free electrons, reducing in a film resistivity, and refining of grains induced by segregation of (Cr, Zr)N and metal-rich phases resulted from a deficiency of nitrogen. Zhang et al. [16] studied corrosion behavior of the film and reported that the chemical inertness could be improved by the additions of Zr into CrN material. Moreover, there are some researches on film color modification by means of stoichiometry and structure adjustments [17–19].

In this work, we reported investigations of crystal structure, cross-sectional and surface morphologies, and chemical information such as chemical compositions, bonding fractions, and chemical states of the CrZrN thin films prepared by reactive DC sputtering. Dependence of these properties on Zr content in the films would be discussed.

2. Experimental details

CrZrN thin films were deposited on 1 × 1 cm^2 silicon (100) wafers and microscope glass slides by using closed field unbalanced DC magnetron co-sputtering system as shown schematically in Fig. 1. The Cr (99.99%) and Zr (99.99%) targets, each with a diameter of 3 in., were used as sputtering sources. The substrates were ultrasonically cleaned in acetone and methanol for 15 min and dried with nitrogen before being installed at a distance of 13 cm from the targets. The chamber

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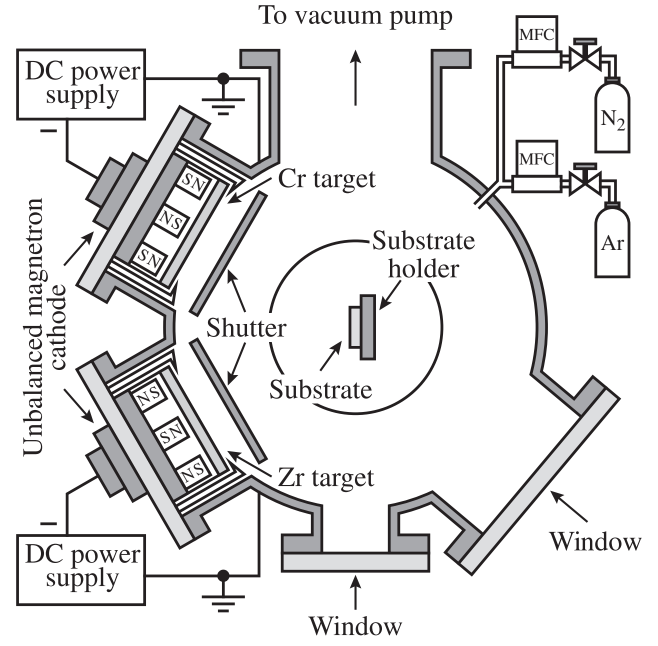

Fig. 1. A schematic diagram of closed field unbalanced DC magnetron co-sputtering system.

was evacuated to achieve a base pressure of about 5×10^{-3} Pa using a pumping system composed of a diffusion pump and a rotary pump. Prior to film deposition, the targets were sputter-cleaned in Ar plasma to remove contaminants for 10 min. An Ar flow rate during the sputter-cleaning was set at 4.0 sccm which regulated a total pressure at about 0.5 Pa, while electrical power on the targets was kept at 0.2 A and ~310 V. After sputter-cleaning of the targets, 99.99% pure N_2 was fed into the chamber at 6.0 sccm whereas Ar was set at 3.0 sccm. With Ar–N_2 mixing, the working pressure was observed to be constant at about 0.4 Pa for all film depositions. The discharge voltage supplied to the Cr target was set to ~325 V to maintain the sputtering current (I_{Cr}) at 0.8 A, whereas the Zr target voltage was varied from 320 to 390 V to achieve the current (I_{Zr}) of 0.2, 0.4, 0.6, and 0.8 A. All the films were deposited for 60 min. In addition, to achieve sputter-deposited films with nanocrystalline structure, the depositions were preformed without applying a bias voltage and an external heat to the substrates [20].

The crystalline structure of CrZrN films was characterized by X-ray diffraction (XRD: Rigaku, Rint 2000) using Cu Kα radiation ($\lambda = 0.1542$ nm). The XRD patterns were recorded at grazing incidence angle of 3° from 20° to 80° of a 2θ range with a scanning speed of $2^\circ\ \text{min}^{-1}$. The cross-sectional morphology was studied by field emission scanning electron microscopy (FE-SEM: Hitachi, S-4700) with the operating voltage of 5.0 kV. The surface morphology was investigated by atomic force microscopy (AFM: Veeco, Nanoscope IV) which operated in the tapping mode on a scanning area of $1 \times 1\ \mu m^2$.

The chemical compositions and chemical states of the CrZrN films were characterized by X-ray photoelectron spectroscopy (XPS: Kratos, AXIS Ultra DLD). Sample surfaces were sputter-cleaned by energetic Ar^+ ions (4 keV and 50 μA) for 60 s to remove contaminants and oxide layer before being irradiated with monochromatic Al Kα X-ray with photon energy of 1486.6 eV to excite atoms on the surface. Wide scanned spectra of the samples were acquired within binding energy (BE) range of 0–1200 eV with pass energy of 80 eV. Areas under background-subtracted peaks of Cr 2p, Zr 3d, N 1s, and O 1s in the spectra were used to determine the elemental concentrations. To study the film chemical states, the high resolution XPS spectra of Cr 2p, Zr 3d, N 1s, O 1s, and C 1s core levels were acquired at narrow BE range with the pass energy of 20 eV. The C 1s spectrum was used as reference for correcting BE shifts caused by charging on the surface during the XPS analysis. The BE of reference for C–C bond in an adventitious carbon used for these samples is 285 eV. After the charge correction and background subtraction, the narrow scanned spectra of Cr 2p, Zr 3d, and N 1 s were deconvoluted to extract the chemical information.

3. Results and discussion

3.1. Chemical composition

XPS wide scanned spectrum of CrZrN thin film with $I_{Zr} = 0.2$ A is shown in Fig. 2. The elements were detected in film surface including Cr, Zr, N, O, and C. In addition to photoemission peaks of the elements, Auger emission lines were found in the spectrum. The wide scanned spectra for the samples with 0.4, 0.6, and 0.8 A of I_{Zr} also showed similar pattern to this figure, but with difference in the peak intensities of each element.

Table 1 lists atomic concentrations of Cr, Zr, N, and O which were determined from the areas of Cr 2p, Zr 3d, N 1s, and O 1s peaks after background subtraction. It was observed that applying higher I_{Zr} resulted in an increase of the number of Zr atoms from 3.74 to 16.58 at.%. Meanwhile, the concentration of Cr atoms was decreased from 48.54 to 34.66 at.% as compared with the increasing Zr content. This result was an effect of using the fixed Cr sputtering current ($I_{Cr} = 0.8$ A) for all film depositions. The detection of O could possibly result from residual gas in the chamber and exposure of the samples to air before the XPS analysis. The O concentration was also decreased from 8.43 to 5.18 at.% as compared to the increasing Zr content. However, the concentration of N atoms increased from 39.37 to 43.59 at.% although the flow rate of N_2 was fixed at 6.0 sccm for all samples. As described in Ref. [21], the increasing of N content could be understood by considering an N-affinity of the two metals from an enthalpy of formation of the CrN and ZrN materials. The enthalpy of formation for CrN solid is −117.15 kJ/mol and that for ZrN is −365.26 kJ/mol [22]. The higher negative value of ZrN suggests that Zr atom has the higher N-affinity and that the ZrN is much easier to form. Moreover, as regards the adsorption process of N_2 molecules on the surfaces of the two metals, it was found that the enthalpy for forming these binary nitrides could lead to an enthalpy of dissociative adsorption for the respective nitrides [23]. As shown in Ref. [24], the enthalpy of dissociative adsorption of N_2 molecules on the surfaces of Ti, Zr, and Hf metals is about −650 kJ/mol which is negatively higher than that of Cr, Mo, and W metals (about −400 kJ/mol). These values indicated that a Zr surface dissociates N_2 and adsorbs nitrogen atoms easier than a surface of Cr metal. For this reason, the increasing Zr content in the films could lead to an increase of Zr surfaces on growing substrate which in turn resulted in the increase of N content. The increase of N also led to an increase of

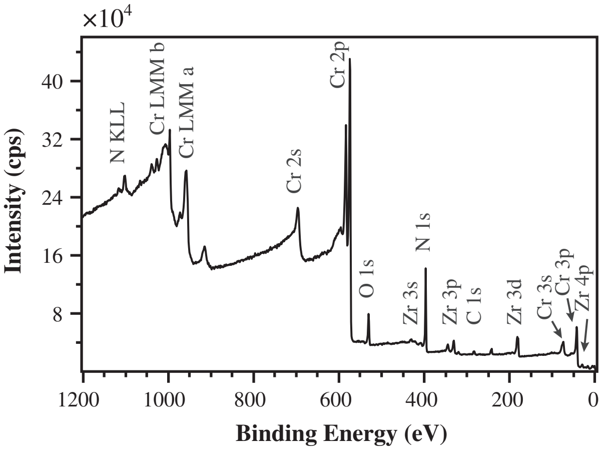

Fig. 2. Wide scanned spectrum of CrZrN thin film with $I_{Zr} = 0.2$ A.