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Argon Irradiation Effects on the Structural and Optical Properties of Reactively Sputtered CrN Films

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Abstract:
The present study deals with CrN films irradiated at room temperature (RT) with 200 keV Ar^+ ions. The CrN layers were deposited by d.c. reactive sputtering on Si (100) wafers, at nitrogen partial pressure of 5×10^{-4} mbar, to a total thickness of 280 nm. The substrates were held at 150°C during deposition. After deposition the CrN layers were irradiated with 200 keV Ar^+ ions to the fluences of 5×10^{15} – 2×10^{16} ions/cm^2. Structural characterization was performed with Rutherford backscattering spectroscopy (RBS), cross-sectional transmission electron microscopy (XTEM) and X-ray diffraction (XRD). Spectroscopic ellipsometry measurements were carried out in order to study optical properties of the samples. The irradiations caused the microstructrual changes in CrN layers, but no amorphization even at the highest argon fluence of 2×10^{16} ions/cm^2. Observed changes in microstructure were correlated with the variation in optical parameters. It was found that both refractive index and extinction coefficient are strongly dependent on the defect concentration in CrN layers.
***Keywords**: CrN films; Ion Irradiation; TEM; RBS; XRD; Ellipsometry.*

1. Introduction

Nitride-based thin films are nowadays widely studied both from fundamental and technological point of views due to their unique physical and mechanical properties [1,2]. Among the binary nitrides, the cubic-base structural chromium-nitride (CrN) is a more recent and interesting choice owing to its well-matched properties to some industrial requirements, especially those that require a hard coating and for tribological applications. This is largely due to the fact that CrN films have a high hardness, high wear- and corrosion-resistance, and also have a low friction coefficient [3,4].

Numerous investigations have been devoted to synthesize CrN coatings via various sputtering and ion-beam-assisted techniques [5–7], e.g. plasma-immersion ion implantation, arc plating, or reactive sputtering, aimed at optimizing the tribological properties. Moreover, many previous studies include ion irradiation as a post-deposition surface treatment for improving the surface properties of thin films [8–9]. It is generally observed that irradiation with noble-gas ions such as Ar, Kr and Xe induces an increase in hardness of the layers [10–11], while the presence of carbon or additional transition metals, such as aluminum, vanadium, zirconium, or molybdenum in coatings, plays an important role and sometimes even improves the tribological features [12–13]. In addition, CrN potentially offers interesting optical properties. Namely, Sikkens et al. [14] reported that CrN layers exhibit excellent spectral selectivity and extremely low emittance and may be applied to solar selective

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absorbers. In this context the effect of 200 keV Ar ions irradiation of the CrN layers was studied.

Our interest here was to study the effects of ion irradiation on the microstructural changes in CrN films, and on the changes of their optical properties. The films were deposited on Si substrates by reactive ion sputtering and subsequently irradiated with argon ions. It was found that ion irradiation rearranges the layer structure, which influences their optical constants.

2. Experimental details

Chromium nitride thin films were deposited by d.c. reactive sputtering from a Cr target of 99.9% purity in a Balzers Sputtron II system, using Ar for sputtering and reactive N_2 gas. The base pressure in the chamber was around 1×10^{-6} mbar, the argon and nitrogen partial pressures during deposition were 1×10^{-3} mbar and 5×10^{-4} mbar, respectively. The substrates used were (100) Si wafers. Before being mounted inside the deposition chamber, the substrates were cleaned in HF solution and in de-ionized water. CrN thin layers were deposited to a thickness of 280 nm at deposition rate of ~10 nm/min. During the deposition, the temperature of the substrates was kept at 150ºC.

After deposition the samples were irradiated with 200 keV Ar^+ ions. The implanted fluences were 5, 10, 15 and 20×10^{15} ions/cm^2 and the implanted area was 2×2 cm^2, homogeneously covered by means of an x-y sweeping system. The beam current was maintained at around 1 μA/cm^2 and all irradiations were performed at room temperature (RT). The irradiation energy was chosen in such a way that the average projected range of the ions was inside CrN layers, according to simulations done with the SRIM code [15]. The projected ion range (R_P) and straggle (ΔR_P) values for 200 keV Ar ions in CrN are 105 nm and 36 nm, respectively.

Structural and optical properties of as deposited and irradiated samples were characterized with Rutherford backscattering spectroscopy (RBS), cross-sectional transmission electron microscopy (conventional - XTEM and high-resolution - HRTEM), X-ray diffraction (XRD) and spectroscopic ellipsometry (SE). The RBS analyses were performed with a 900 keV He^{++} ion beam provided by the IONAS implanter in Göttingen [16] with two Si-surface barrier detectors positioned at a 165º backscattering angle. The backscattering spectra were taken at normal incidence and the changes in the concentration profiles of the CrN/Si components were analyzed with the WiNDF code [17]. Cross-sectional TEM was done on a JEOL 100CX microscope, using 100 kV electron beam. HRTEM measurements of some selected samples were performed by means of a Philips CM200-FEG microscope, operated at 200 keV, and we also used fast Fourier transformation (FFT) analyses. All the samples were analyzed by X-ray diffraction with a BRUKER D8 Advance diffractometer by using the CuK_α radiation and scanning the 2θ range between 30º and 65º. From a broadening of the characteristic peaks, the lattice constants, the crystallites size and strain of the CrN thin films were determined. SE measurements were recorded within a HORIBA – Jobin Yvon UVIS ellipsometer at 70º angle of incidence. The measurements were carried out in ambient air in the photon energy range of 0.6 – 4.8 eV (260 – 2100 nm) with steps of 0.1 eV. The data analysis was performed using Delta Psi2 software which was provided with the instrument.

3. Results and discussion

3.1 RBS analyses

In a first step, compositional analyses using RBS measurements indicated the growth of stoichiometric CrN layers deposited at nitrogen partial pressure of 5×10^{-4} mbar and substrate temperature at 150ºC. Fig. 1 shows a set of the Cr depth profiles in CrN layers, as deduced by means of WiNDF code [17], taken from as deposited layer and the samples irradiated with 200 keV Ar ions to the fluences of 5×10^{15} and 2×10^{16} ions/cm^2. The evaluation of Cr profiles provide precise information on composition, the Cr to N ratios were consistently ~1:1 over the whole layers thickness. It should be also noted that in as deposited state concentration of argon was found to be ~2 at.% throughout CrN layer (shown in subFig.), showing a low contamination level of the layers during the deposition process. After implantation the concentration of argon increases, reaching about 5 at.% for the highest implanted fluence. Note that the SRIM calculations [15] gave a mean projected R_p= 105 nm and a straggling of ΔR_p= 36 nm for the above irradiation parameters. Analyses indeed show that the Ar ions concentration profiles and the depth where ions are stopped in the irradiated samples are very close to the SRIM values.

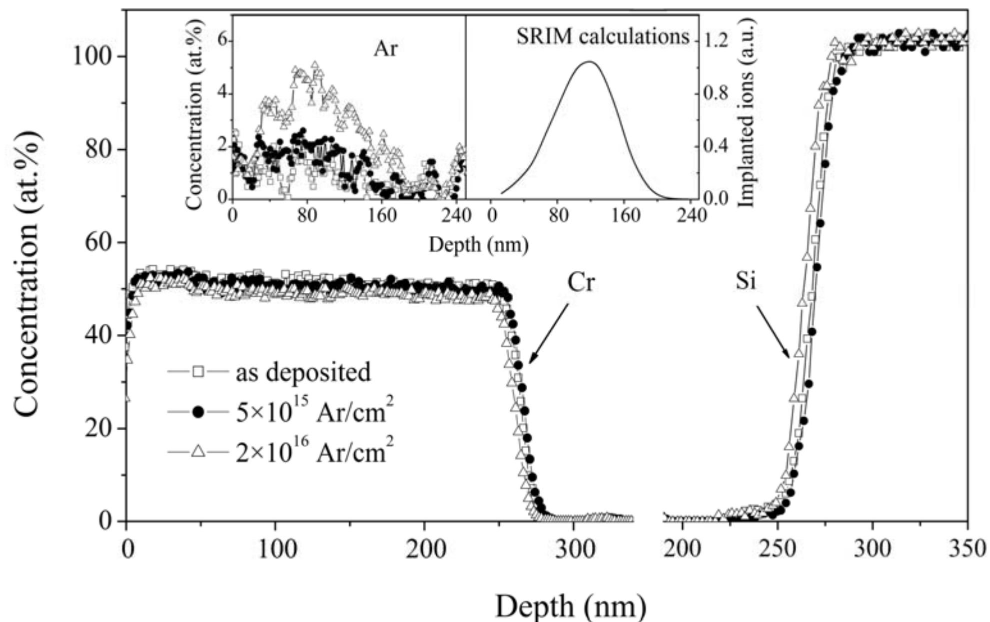

Fig. 1. Concentration profiles of Cr and Si in CrN films obtained from RBS spectra taken after deposition and after irradiation with 5×10^{15} and 2×10^{16} Ar/cm^2. Depth profiles of Ar are given in the inset.

3.2 XRD analyses

The phase evaluation of the as deposited and irradiated CrN layers where analyzed by X-ray diffraction, as shown in Fig. 2(a-c). Fig. 2a depicts relative intensities of as deposited sample. The spectrum consists of the (111) and (200) cubic peaks centred at 2θ = 37.44º and 2θ = 43.67º, respectively. A relatively weak reflection from (311) phase was also observed, so for clarity is not presented in the Fig.. In the samples irradiated with 200 keV Ar ions to 5×10^{15} ions/cm^2 (b) and 2×10^{16} ions/cm^2 (c), the position of the main Bragg reflections gradually shifted toward lower diffraction angles, as the Ar ions fluence was increased. More precisely, this is an indication of an increase in the lattice parameters of the formed nitride.

This can be interpreted in the frame of the stress-related effects and damage induced by Ar ions irradiation.

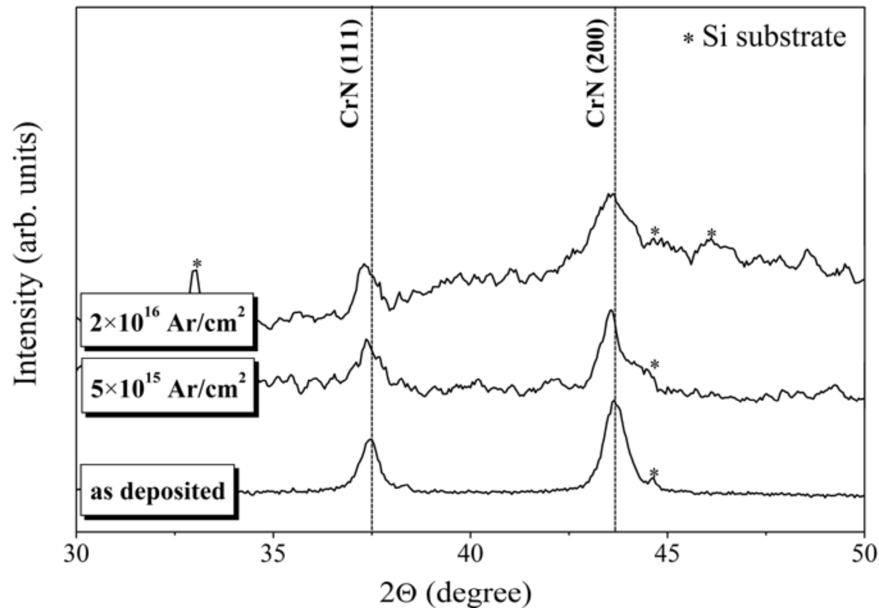

Fig. 2. XRD spectra of as deposited CrN layer and samples irradiated with 200 keV Ar ions.

In order to further qualify the microstructural changes occurring during ion irradiation, we calculate lattice constants, micro-strain and crystallite size of the CrN thin films. The variation of the lattice constants and micro-strain with ion fluence is shown in Fig. 3. As can be seen the lattice parameters of CrN after Ar ions irradiation to 5×10^{15} ions/cm^2 is slightly higher than that of the values for as deposited samples because of the damage and stress generated in the films. The lattice parameters remain constant after irradiation with the higher ion fluence of 2×10^{16} ions/cm^2, suggesting that the stress relaxation and the relief of point defects are pronounced. Indeed, the micro-strain increases when increasing ion fluence, with observed deviation in the case of (200) reflection for irradiation to 5×10^{15} ions/cm^2.

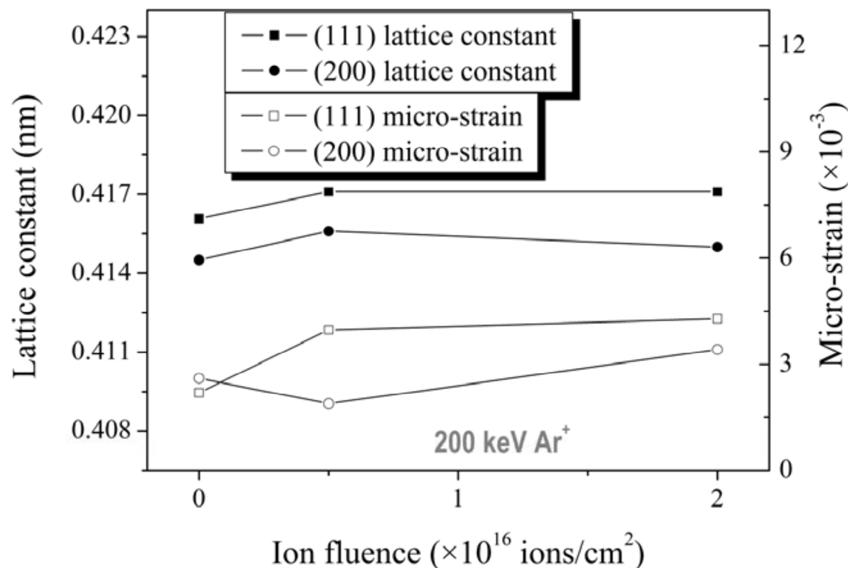

Fig. 3. Variation of the lattice constant and micro-strain of CrN films, as a function of Ar ion fluence.

Tab. I Summary of the structural parameters calculated for as deposited and 200 keV Ar ions irradiated CrN thin films.

Sample	Miller indices (hkl)	Lattice constant (nm)	Micro-strain ($\times10^{-3}$)	Mean grain size (nm)
as deposited	(111)	0.4161	2.20	14
	(200)	0.4145	2.61	
5×10^{15} Ar/cm^2	(111)	0.4171	4.00	13
	(200)	0.4156	1.90	
2×10^{16} Ar/cm^2	(111)	0.4171	4.29	9
	(200)	0.4150	3.42	

Obviously this can be due to different relief of point defects of (111) and (200) reflections. In addition, the mean grain size in the CrN films was estimated from the full width at half maximum (FWHM) of the X-ray diffraction lines using Scherrer`s formula [18]. The mean crystallite size was found to be ~14 nm, ~13 nm and ~9 nm for the as deposited sample and the samples irradiated with Ar^+ ions to 5×10^{15} ions/cm^2 and 2×10^{16} ions/cm^2, respectively. Finally, the values of the lattice constant, mean grain size and micro-strain obtained for all samples are summarized in Tab. I.

3.3 TEM-HRTEM analyses

In order to investigate the microstructural evolution in the CrN films, TEM cross sectional analyses of the samples irradiated with argon ions were performed. Fig. 4 shows the cross sectional bright field image (a) and high resolution image (b) of the sample irradiated with 200 keV argon ions to 2×10^{16} ions/cm^2.

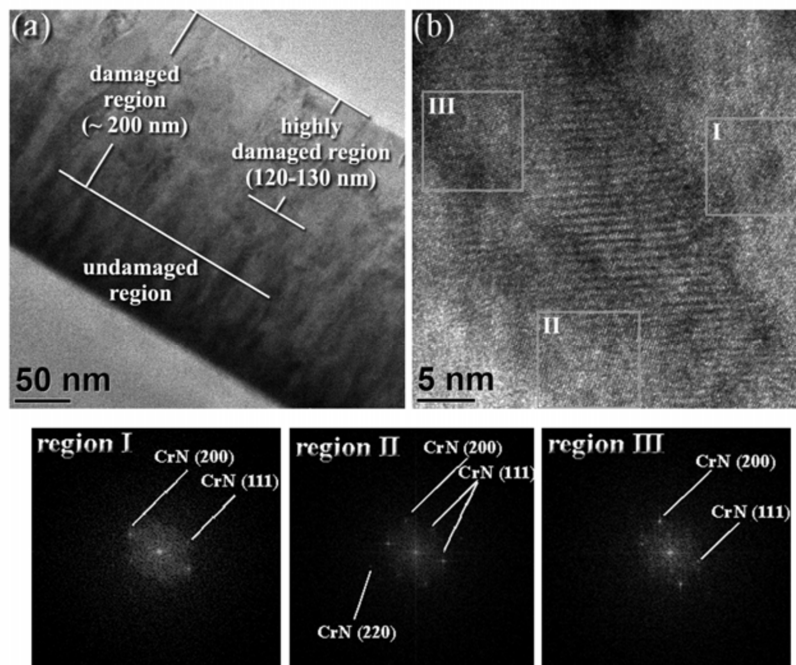

Fig. 4. XTEM analysis of the CrN/Si sample implanted with 2×10^{16} Ar/cm^2: (a) bright field image; (b) high-resolution image; (c) Fourier transforms from regions labeled as I, II, and III in (b).

The Fourier transforms taken from different regions of the high resolution image are also presented in the Fig. 4. Closer analysis reveals that there are three regions as indicated on the low magnification bright field image. They represent the positions of the undamaged region, damage region of ~200 nm thick and highly damaged region ~120-130 nm thick, respectively. The bottom layer, which is labeled as undamaged region i.e., as deposited layer it was found that has a well-grown crystalline phase with a columnar structure. Note that the bottom layer which can be easily distinguished from the damaged regions by image contrast makes up approximately 30% of the total layer thickness. From high resolution image obtained in the top high damage region and corresponding Fourier transforms it follows that this layer consists of CrN phase. As an example, Fig. 4b show the layer structure with areas of agglomerated defects and Fourier transforms from these localized regions labeled as I, II and III, respectively. The Fourier transforms shows reflections corresponding to (111), (200) and (220) planes of CrN. Hence, we may conclude that crystallographic data are fully consistent with CrN phase. In addition, the analysis indicates a substantial amount of disorder but not the presence of an amorphous phase in the damaged region.

3.4 Spectroscopic ellipsometry

The refractive indices (n) and extinction coefficients (k) of modified CrN layers obtained by SE measurements for different Ar ions fluences are shown in Fig. 5a and b, respectively. It is observed that the refractive index values (Fig. 5a) are higher in the low-energy region and show normal dispersion as the photon energy increases. As the Ar ion fluence increases the layers become optically less dense.

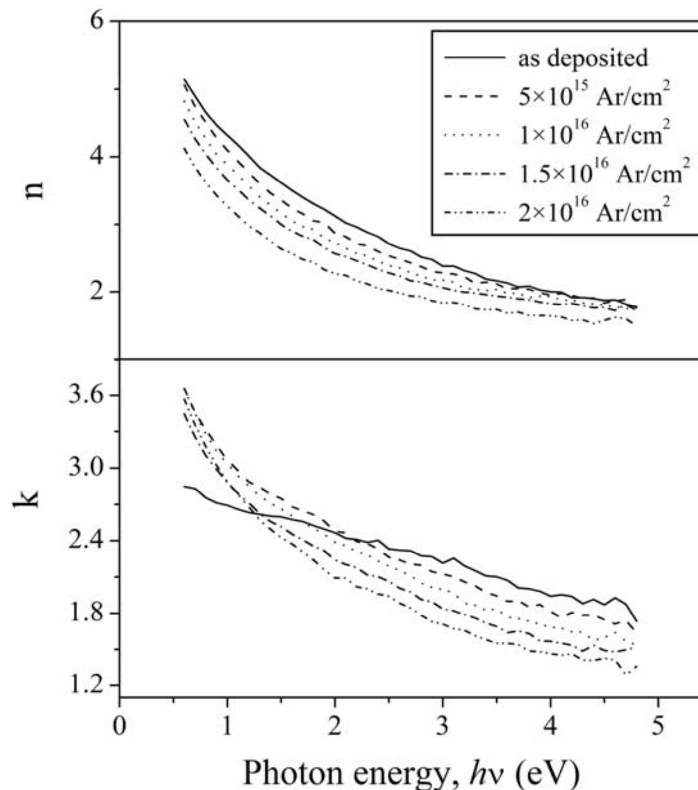

Fig. 5. Optical properties of of as deposited and Ar irradiated CrN layers as a function of photon energy: (a) refractive indices-n; (b) extinction coefficients-k.

Their refractive index decreases, and for example at hν = 3 eV is 2.38, 2.28 and 1.84 for as deposited, 5×10^{15} ions/cm^2 and 2×10^{16} ions/cm^2 layers, respectively. Moreover, the optical

constant decreases more quickly in the infrared region when the argon fluence increases. We think that the increase in defects concentration in CrN films and the reduction in grains size (Tab. I), which reduce the electrons mean free path, is at the origin of this behavior. Thus the refractive index of the treated layers is directly proportional to the ion fluence, i.e. to the total number of the implanted ions. A similar but somewhat different dependence is observed for the extinction coefficient of the treated layers (Fig. 5b). The extinction coefficient of the CrN films decreases with the Ar ion fluence at higher photon energy values. We notice, however, that the k parameter is less sensitive to the variation of irradiation fluence in the infrared region, and all spectra exhibit higher values as compared to the values of as deposited sample. Both refractive index and extinction coefficient found to be comparable with those obtained for CrN films prepared by ion beam assisted deposition process [19].

4. Conclusions

In the present study, we have investigated the changes of the microstructure and optical properties of CrN thin films induced by 200 keV Ar ions irradiation. From the RBS analyses, it was found that after irradiation a uniform stoichiometric composition (~1.0) of the CrN layers remains unchanged. The XRD results showed that irradiation resulted in increase of the lattice constants of the CrN films. Irradiation also resulted in increase of the micro-strain of the layers. Observed variation of the lattice constants, mean grain size and micro-strain can be attributed to the formation of the high density damage region in the CrN film structure. XTEM results revealed that this damage region is mainly distributed within ~120-130 nm at surface of the layers. Generally, these structural changes lead to a decrease of both refractive index and extinction coefficient, which can be correlated to an increase in defect concentration induced by Ar ions.

Acknowledgments

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Садржај: *У овом раду су приказани резултати испитивања својстава танких слојева CrN бомбардованих са 200 keV* Ar^{+} *јонима, у условима собне температуре. Танки слојеви CrN су депоновани методом реактивног распрашивања до дебљине од ~280 нанометара, при парцијалном притиску азота од* 5×10^{-4} *mbar. Као подлоге за депоновање су коришћене монокристалне силицијумске плочице оријентације (100). Температура подлоге у току депоновања је одржавана на ~150 ºC. Након депоновања CrN слојеви су имплантирани са 200 keV* Ar^{+} *јонима у опсегу доза од* 5×10^{15} 2×10^{16} *jona/cm*^{2}*. Структурна својства узорака су испитивана методом Rutherford-овог повратног расејања, трансмисионом електронском микроскопијом и дифракцијом X-зрачења. За испитивање оптичких својстава слојева коришћена је метода спектроскопске елипсометрије. Уочено је да је након имплантације дошло до микроструктурних промена у CrN слојевима, али не и до аморфизације, чак ни у случају највеће дозе имплантације од* 2×10^{16} *jona/cm*^{2}*. Уочене микроструктурне промене су доведене у везу са променама оптичких параметара слојева. Нађено је да индекс преламања и коефицијент екстинкције директно зависе од концентрације дефеката у CrN слојевима.*
Кључне речи: *Танки слојеви CrN; јонска имплантација; трансмисиона електронска микроскопија; Rutherford-ово повратно расејање; дифракција X-зрачења; елипсометрија*