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A study on the high rate deposition of CrN_x films with controlled microstructure by magnetron sputtering

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Abstract

High rate deposition of CrN_x films with control of microstructure was carried out by magnetron sputtering. For these purposes, the deposition processes parameters were varied: N_2 flow rate and especially substrate bias voltage, duty cycle and frequency using a pulsed DC power supply. The microstructure was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and mechanical properties were evaluated by a microhardness test and adhesion test. The maximum deposition rate for CrN_x compound films could be reached to nearly 90% compared with that for pure Cr coating due to the increase of ionization efficiency caused by a negative-pulsed DC bias. As N_2 flow rate is increased, the microstructure of CrN_x films was changed from $Cr + Cr_2N$ to CrN. Also, a phase transformation occurred between Cr_2N + CrN multi-phase and CrN mono-phase by control of a negative DC and/or pulsed DC bias voltage, duty cycle and frequency. Microhardness for CrN_x films were measured to be up to 1600 kg/mm^2 and the maximum hardness value of 2250 kg/mm^2 was obtained for CrN_x film deposited with a N_2 flow rate of 20 sccm at a negative DC bias of -100 V. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: CrN_x; Magnetron; Deposition rate; Microstructure; Pulsed DC bias

1. Introduction

High rate deposition processes such as high current arc, laser arc, hollow cathode discharge ion plating and magnetron sputtering methods have been developed for cost effective industrial applications [1–3]. Especially magnetron sputtering is emerging as a very efficient method for the synthesis of high rate deposited dense films. In the early years of the 1990s a deposition rate of $1 \sim 3$ μm/min has been reached using an unbalanced magnetron, but these have been restricted to pure metal films such as Cu, Ag, etc., of high sputtering yield. Overcoming a poisoning effect between metallic targets (Ti, Cr, etc.) and reactive gases (N_2, O_2, etc.), high rate deposition of reactively sputtered nitride and oxide films by reactive magnetron sputtering have been realized to the deposition rate of $60 \sim 70\%$ compared with that of pure metals by precise partial pressure control of the reactive gas [4,5]. In the mean time, the correlations between process parameters, microstructure and film properties have also been intensively studied to ensure the reproducibility of films with pre-defined properties [6–8]. In case of nitride films, particularly, it has been reported that the main parameters controlling the film microstructure are deposition temperature, N_2 partial pressure and bias voltage [6,7,9].

In this study, an unbalanced magnetron sputtering was employed to synthesize CrN_x films for high rate deposition with a control of microstructure. Deposition processes for such purpose were varied with N_2 flow rate and specially substrate bias voltage, duty cycle and frequency using pulsed DC power supply. The microstructure was analyzed by X-ray diffraction (XRD)

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and scanning electron microscopy (SEM), and mechanical properties were evaluated by microhardness and adhesion tests.

2. Experimental details

2.1. Film deposition

CrN_x films were deposited on AISI 304 stainless steel and Si wafers by magnetron sputtering of a rectangular Cr target with a moving magnet designed for high erosion efficiency, in our laboratory. The discharges of this magnetron, which are elliptically shaped with the longer axis perpendicular to the longer axis of the target, are generated by separated magnetic units placed behind the target. Non-sputtered regions inside the individual racetracks are eliminated by the simultaneous sweeping of all magnetron discharges along the longer axis of the target, which is achieved by moving the magnetic means behind the target. All specimens were cleaned following conventional cleaning process prior to deposition. The deposition process was performed in the following steps: (1) radiation heating; (2) DC glow discharge cleaning in an Ar atmosphere for 10 min; (3) sputter deposition of a 0.2 μm Cr interlayer film; (4) deposition of CrN_x films at various conditions listed in Table 1.

2.2. Evaluation of films

For the evaluation of phase and texture formation for CrN_x films XRD analyses were performed with an incident angle of 3°. By using SEM fracture cross-sectional morphologies were investigated and the deposition rate of coated samples was calculated. Micro Knoop hardness was measured at a normal load of 0.025 N. The adhesion strength was compared by observing the propensity for cracks and the degree of delamination near the indentation periphery using an optical microscope after Rockwell C indentation test.

Table 1
Conditions for CrN_x coating process

Deposition parameters	Conditions
Base pressure	3×10^{-5} torr
Ar pressure	1.8×10^{-3} torr
Target power density	13 ± 1 W/cm^2 (DC)
Distance between target and substrate	80 mm
Temperature	400 ± 10°C
N_2 flow rate	0 ~ 45 sccm
Substrate bias (pulsed DC)	
Voltage (V)	−50, −100, −200
Duty cycle (%)	50, 70, 100
Frequency (kHz)	5, 10, 20

3. Results and discussion

3.1. Influence of N_2 flow rate

Fig. 1 shows XRD patterns of CrN_x films deposited on Si wafer with various N_2 flow rates at a negative DC bias of −100 V. At a N_2 flow rate of 20 sccm, a mixed phase containing Cr(110), CrN(200) and $Cr_2N(111)$ was observed. As N_2 flow rate is further increased upon

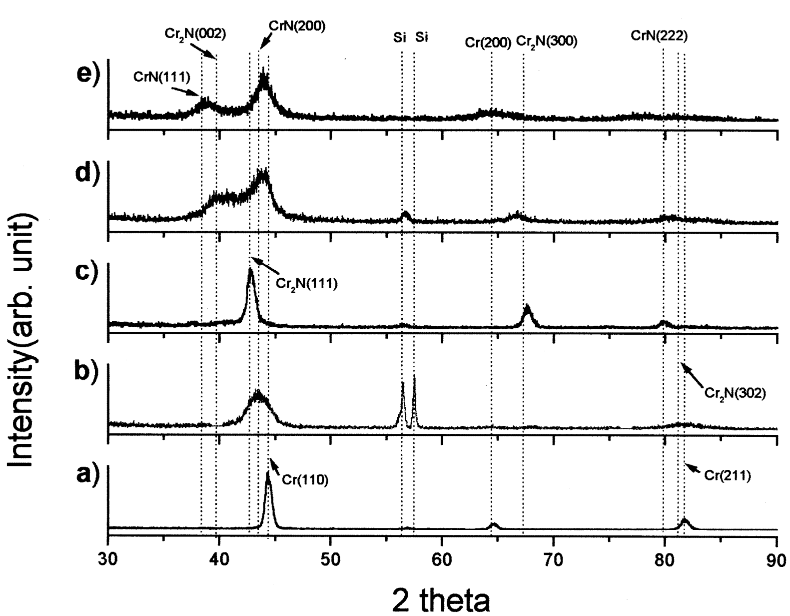

Fig. 1. XRD patterns of CrN_x films deposited on Si wafer with various N_2 flow rates. (a) 0 sccm, (b) 20 sccm, (c) 30 sccm, (d) 40 sccm and (e) 45 sccm.

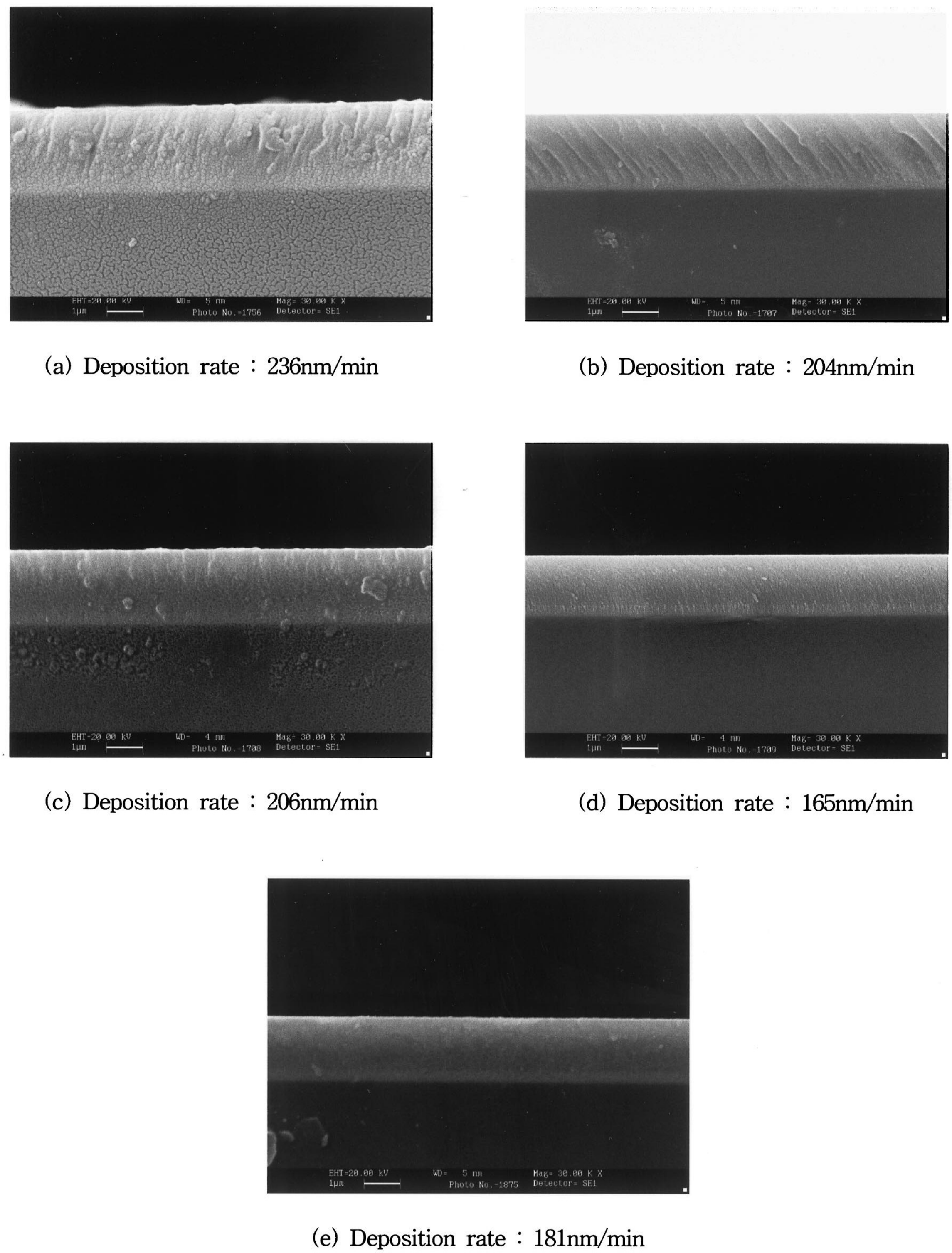

Fig. 2. Cross-sectional scanning electron micrographs of CrN_x films deposited on Si wafer with various N_2 flow rates. (a) 0 sccm, (b) 20 sccm, (c) 30 sccm, (d) 40 sccm and (e) 45 sccm.

deposition, CrN_x films tend to change from the hexagonal Cr_2N phase to the cubic CrN phase. The CrN_x film deposited with N_2 flow rate of 30 sccm was formed mostly with Cr_2N mono-phase and then transformed to CrN mono-phase with a further increase of the N_2 flow to 45 sccm.

The SEM micrographs of fractured cross-sections of the films are illustrated in Fig. 2. It shows that the

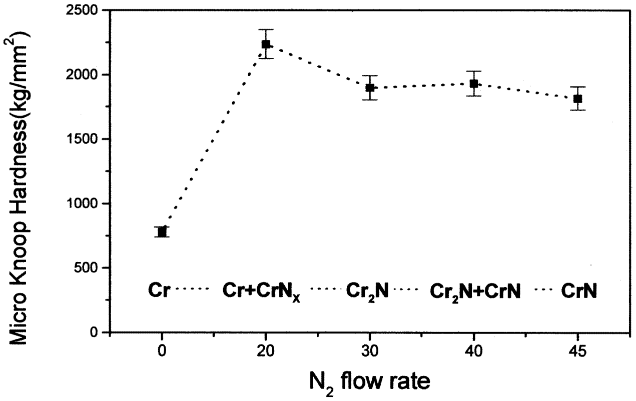

Fig. 3. Microhardness changes of CrN_x films measured at normal load of 0.025 N for various N_2 flow rates.

increasing of N_2 flow rate leads to an increase of film density and the decrease of its deposition rate from 236 to 165nm/min except for CrN_x film deposited with a N_2 flow rate of 45 sccm. This reduction of deposition rate is due to the formation of chromium nitride at the target surface, the so called 'poisoning effect' [4,5].

Fig. 3 illustrates the microhardness of CrN_x films deposited with various N_2 flow rates. The maximum hardness value of 2250 kg/mm^2 was obtained for CrN_x film deposited with a N_2 flow rate of 20 sccm while further increase of the N_2 flow rate up to 45 sccm tended to reduce the hardness in the range of 1800–2000 kg/mm^2. These results are somewhat different from other reports in which the maximum hardness value was obtained for Cr_2N mono-phase [10,11]. It is estimated that the mixing effect [12] between Cr, Cr_2N and CrN plays a role to improve hardness of CrN_x film deposited with N_2 flow rate of 20 sccm. And also the reason why the similar hardness value was obtained for Cr_2N film deposited with N_2 flow rate of 30 sccm compared with CrN films is predicted that this film was consist of not only Cr_2N phases but also CrN phases as shown in Fig. 1.

After results of Rockwell C indentation adhesion tests, all CrN_x films deposited with various N_2 flow rates persisted in fairly good adhesion with a little crack and delamination corresponding to HF1 ~ HF3 in terms of the German short form of adhesion strength [13,14].

3.2. Influence of substrate bias

For the understanding of substrate bias effect influenced CrN_x film properties CrN_x films were deposited with various substrate bias voltage, duty cycle and frequency using pulsed DC power supply at constant N_2 flow rate of 40 sccm. Table 2 illustrates sample name and summary of the substrate bias effect on the deposition rate, microhardness and adhesion strength of CrN_x films. Moreover, the microstructure of each coated sample was identified in Fig. 4 by XRD analyses. The microstructure of CrN_x film deposited with a negative DC bias voltage of −100 V (CrN-2) was defined to be $Cr_2N + CrN$ multi-phase. However, this multi-phase was changed to Cr_2N mono-phase(CrN-1, 3) when the substrate bias voltage was varied. Also, the variation of pulse frequency at a duty cycle of 70% led to the phase transformation from Cr_2N mono-phase (CrN-5) to $Cr_2N + CrN$ multi-phase (CrN-4, 6), and then Cr_2N mono-phase (CrN-5) was changed to $Cr_2N + CrN$ multi-phase (CrN-7) with the decrease of duty cycle at the same frequency. These phase transformations with the change of substrate bias is due to nearly equal energy of formation between Cr_2N (−122.88 kJ/mol) and CrN (−123.98 kJ/mol) at 400°C with constant N_2 partial pressure [10]. Two different phases, CrN and Cr_2N, which have very closed value of free energy of formation have almost same probability to nucleate and grow. Thus, these two phases might independently nucleate depending on the adatom energy state which is strongly influenced by substrate bias when other deposition parameters such as power density of target, substrate temperature and N_2 flow rate were the same.

At a negative bias voltage with sufficient duty cycle and frequency (CrN-5, 6), respectively, the deposition rate was increased. It is estimated that the ionization efficiency was increased by repetitive impact and stagnation between adatoms caused by a negative pulsed DC bias [15]. The maximum deposition rate of 210

Table 2
Sample identification and summary of the substrate bias effect

Sample	Duty cycle (%)	Frequency (kHz)	Bias voltage (V)	Deposition rate (nm/min)	Microhardness (kg/mm^2)	Adhesion strength
CrN-1	100	–	−50	174	1631	HF3 ~ 4
CrN-2	100	–	−100	165	1930	HF1 ~ 2
CrN-3	100	–	−200	194	2099	HF1 ~ 2
CrN-4	70	5	−100	162	2044	HF2 ~ 3
CrN-5	70	10	−100	210	2037	HF1 ~ 2
CrN-6	70	20	−100	180	2063	HF1 ~ 2
CrN-7	50	10	−100	163	1599	HF3 ~ 4

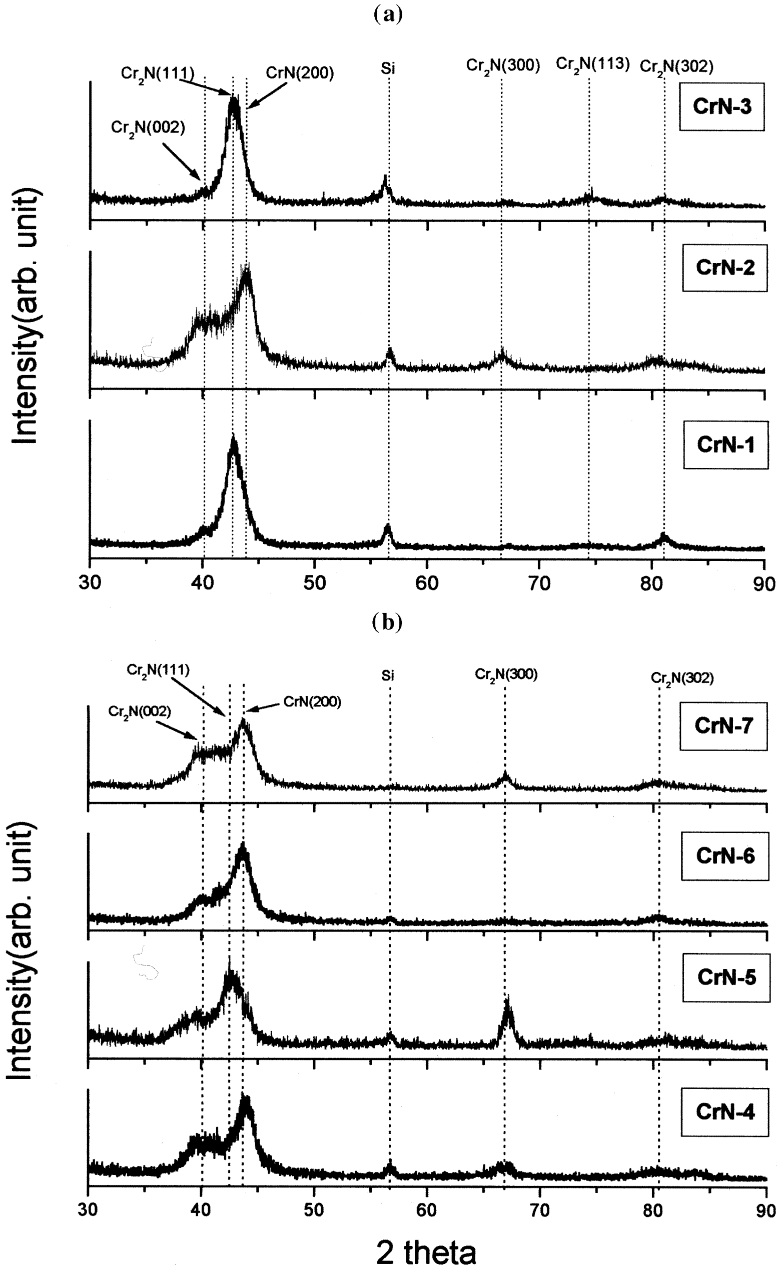

Fig. 4. XRD patterns of CrN_x films deposited on Si wafer at N_2 flow rate of 40 sccm with (a) various substrate bias voltages and (b) various substrate bias duty cycles and frequencies.

nm/min was obtained for CrN-5, which is 89% compared with the deposition rate of pure Cr coating under the same conditions except for a negative-pulsed DC duty cycle.

The microhardness of CrN_x films were measured to be similar values independent of the microstructure except for CrN-1 and CrN-7 which were deposited with low bias voltage or duty cycle. It has been reported [16,17] that the low bias voltage or duty cycle leads to a decrease of microhardness of films due to decreasing adatom mobility. After results of adhesion tests by Rockwell C indentation, CrN-1 and CrN-7 were proved to be HF3 ~ 4 while other films have a good adhesion strength corresponding to HF1 ~ 3. The low adhesion of CrN-1 and CrN-7 is understood by the decrease of ion bombardment caused by low adatom mobility during processes.

4. Summary

The high rate deposition of CrN_x films was carried out by magnetron sputtering with controlled microstructure. In this study, the following results have been obtained:

1. The maximum deposition rate for CrN_x compound films was reached to 89% compared with that for pure Cr coating due to the increase of ionization efficiency caused by a negative pulsed DC bias.
2. The microstructure of CrN_x films could be successfully controlled with by variation of the negative bias voltage, duty ratio and frequency as well as the N_2 flow rate.
3. Microhardness for CrN_x films were measured to be more than two times of that for Cr coating and the maximum hardness value of 2250 kg/mm^2 was obtained for CrN_x film deposited with the N_2 flow rate of 20 sccm at a negative DC bias of −100 V.

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