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# TEM study of crystalline structures of Cr–N thin films

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Cr–N films were grown on Si (001) substrates by reactive magnetron sputtering under an N<sub>2</sub>/Ar atmosphere at room temperature. The composition of the films, expressed as Cr<sub>1-x</sub>N<sub>x</sub>, can be varied by changing the N<sub>2</sub>/Ar pressure ratio during the synthesis process. Crystalline states of Cr–N films have been studied using electron diffraction. It is well known that two intermediate phases, Cr<sub>2</sub>N (hexagonal) and CrN (cubic), exist in the Cr–N system, and small variations around the ideal stoichiometry are tolerated. The present study shows that cubic CrN with vacancies rather than hexagonal Cr<sub>2</sub>N may exist in a Cr–N film with a thickness of about 50 nm produced under a low N<sub>2</sub> partial pressure.

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## 1. Introduction

According to the phase diagram of the Cr–N system (Venkatraman & Neumann, 1990), the Cr<sub>2</sub>N phase is stable with a nitrogen composition range of about 27.5–33 at.%, and CrN has a very narrow equilibrium range (47.5–50 at.% N). As important coating materials, Cr–N thin films have been studied continuously. The results show that the formation of CrN or Cr<sub>2</sub>N phases mainly depends on the nitrogen partial pressure,  $P_{N_2}$ . Reactive sputtered Cr–N films consist of the CrN phase at a relatively high nitrogen partial pressure and the Cr<sub>2</sub>N phase at a relatively low nitrogen partial pressure, although the reported nitrogen partial pressures were not exactly the same owing to various other experimental conditions (Ehrlich *et al.*, 1995; Hones *et al.*, 1997, 2003; Inoue *et al.*, 2002).

CrN has a face-centered cubic (f.c.c.) structure ( $a = 0.414$  nm) while Cr<sub>2</sub>N has a hexagonal structure ( $a = 0.4752$  nm and  $c = 0.4429$  nm) (Villars & Calvert, 1985). The CrN phase is antiferromagnetic, with a Néel temperature ( $T_N$ ) of around 280 K; the magnetic properties of Cr<sub>2</sub>N are not clear, although it has been reported not to be ferromagnetic in the temperature range 85–500 K (Browne *et al.*, 1970).

Our research on Cr–N films originated from studying Cr-doped AlN (AlCrN), a ferromagnetic semiconductor system (Zhang *et al.*, 2004). To clarify the origin of the ferromagnetism, we must exclude the contributions from any possible second phases in AlCrN, including CrN and Cr<sub>2</sub>N. Therefore, the structure and properties of Cr–N films were studied. We report here the structural characterization of these films through transmission electron microscopy (TEM).

## 2. Experimental methods

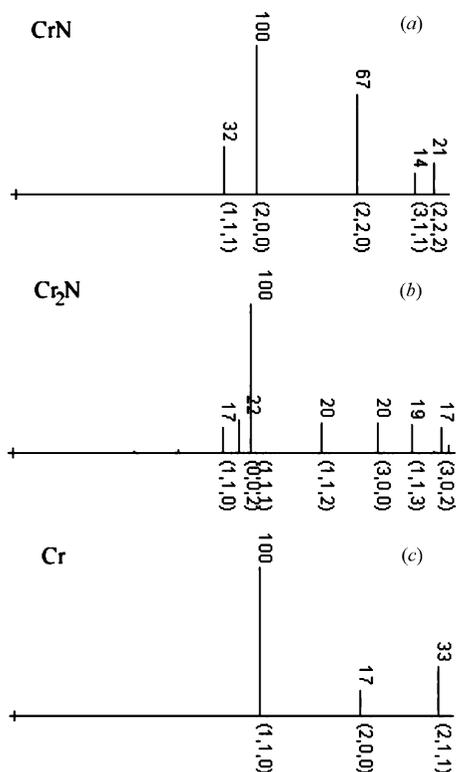
Cr–N films were grown on Si (001) substrates by reactive magnetron sputtering under an N<sub>2</sub>/Ar atmosphere at room temperature. The discharge power was kept constant at 40 W, and the distance between the substrate and the target was fixed at 9 cm. The residual pressure was in the region of  $6 \times 10^{-5}$  Pa before the introduction of the sputtering gases. During film growth, the Ar pressure was fixed at  $5 \times 10^{-1}$  Pa and two different N<sub>2</sub> partial pressures were employed,  $P_{N_2} = 5 \times 10^{-1}$  Pa and  $P_{N_2} = 3 \times 10^{-3}$  Pa; the corresponding samples are

labeled hereafter as samples 1 and 2, respectively. The film thickness was about 50 nm. The films were first checked with X-ray diffraction methods (Rigaku diffractometer with Cu  $K\alpha$  radiation), but no obvious diffraction peaks were observed. TEM specimens were prepared by mechanical polishing followed by ion milling on a Gatan PIPS. Electron diffraction experiments were carried out on a JEM2010 transmission electron microscope. Simulation of polycrystalline electron diffraction was carried out using the computer program *JECPIPCED* (Li, 2004).

## 3. Results and discussion

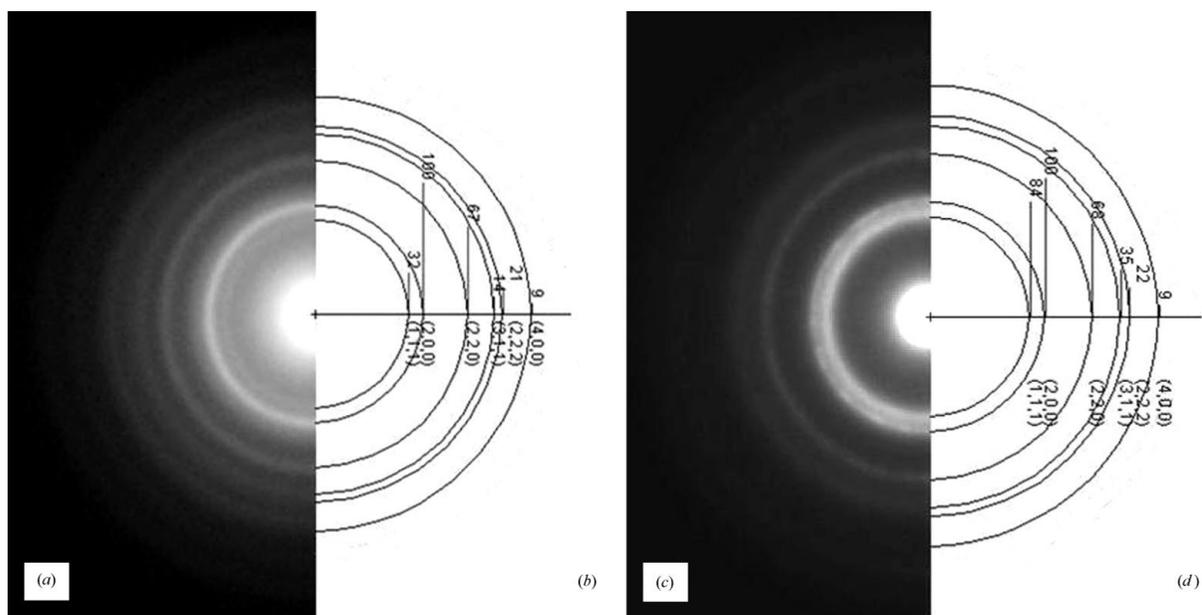
Microcrystalline phases in two types of samples were observed in the TEM experiment; thus polycrystalline electron diffraction patterns were obtained for phase identification. Fig. 1 shows the calculated polycrystalline electron diffraction patterns of the structures of (a) the f.c.c. CrN phase (Villars & Calvert, 1985), (b) the hexagonal Cr<sub>2</sub>N phase (Kim *et al.*, 1990) and (c) b.c.c. Cr. The calculated patterns show that it should be possible to distinguish the CrN, Cr<sub>2</sub>N and Cr phases by their polycrystalline electron diffraction patterns.

Fig. 2 shows (a) a polycrystalline electron diffraction pattern taken from sample 1 and (b) a simulated pattern calculated on the basis of the structure of the f.c.c. CrN phase. Both the radii of the rings and their relative intensities are in good agreement, confirming that the microcrystalline phase in sample 1 is the f.c.c. CrN phase. Fig. 2(c) shows a polycrystalline electron diffraction pattern taken from sample 2. The simulated patterns (see Figs. 1b and 1c) of the hexagonal Cr<sub>2</sub>N phase and Cr do not fit the experimental pattern. The radii of the rings in the experimental pattern are the same as those in Fig. 2(a), although the relative intensities of corresponding rings are different. Therefore, the microcrystalline phase in sample 2 should have the same or a very similar type of unit-cell and lattice parameters. Considering the fact that sample 2 was synthesized under a low N<sub>2</sub> partial pressure compared with that used for sample 1, we tried to use the structure of the cubic CrN phase with vacancies to interpret Fig. 2(c). A simulated pattern is shown in Fig. 2(d), which is calculated using the structure of the cubic CrN phase with half occupancy at N sites. This figure shows that the intensity of the inner-



**Figure 1**  
Comparison of calculated polycrystalline electron diffraction patterns of (a) f.c.c. CrN, (b) hexagonal Cr<sub>2</sub>N and (c) b.c.c. Cr, with intensities on top and indices at the bottom of each peak.

most ring is dramatically increased while the intensities of other rings do not change very much. The simulated pattern in Fig. 2(d) can be used to match to the experimental one in Fig. 2(c); thus, the microcrystalline phase in sample 2 can be interpreted as the cubic CrN phase with vacancies at the N sites.



**Figure 2**  
Experimental polycrystalline electron diffraction patterns of thin films produced (a) with N<sub>2</sub> partial pressure  $P_{N_2} = 5 \times 10^{-1}$  Pa and (c) with N<sub>2</sub> partial pressure  $P_{N_2} = 3 \times 10^{-3}$  Pa. Simulated patterns (b) based on the cubic CrN structure and (d) based on the cubic CrN structure with half occupancy of N sites.

Hones *et al.* (1997) have shown that the nitrogen partial pressure strongly influences the crystal structure and morphology of Cr–N deposited films. In films deposited at room temperature and a thickness of 550 nm, CrN is formed if  $P_{N_2} > 0.16$  Pa. The pure Cr<sub>2</sub>N phase is not observed, whereas mixed Cr–Cr<sub>2</sub>N and Cr<sub>2</sub>N–CrN phases are observed in wide ranges of concentrations. More recently, Hones *et al.* (2003) have deposited very thin films (8–20 nm) on a carbon grid and analysed them by high-resolution electron microscopy. The crystallized matrix of Cr<sub>2</sub>N grains is embedded in the poorly crystallized matrix of f.c.c. CrN. It has been suggested that, at least in the early growth stage, randomly distributed nitrogen vacancies in the CrN matrix diffuse towards the Cr<sub>2</sub>N nuclei.

Inoue *et al.* (2002) have shown that the nitrogen concentration in the Cr–N films increases rapidly with increasing  $P_{N_2}$  up to  $1.5 \times 10^{-2}$  Pa, and is then almost unchanged at pressures of up to  $1.5 \times 10^{-1}$  Pa. For as-deposited Cr–N films with a thickness of about 300 nm, when  $P_{N_2}$  is between  $4.5 \times 10^{-4}$  and  $1 \times 10^{-2}$  Pa, the hexagonal Cr<sub>2</sub>N phase appears and the diffraction peaks become weaker with increasing  $P_{N_2}$ . At  $P_{N_2} > 1 \times 10^{-2}$  Pa, the f.c.c. CrN phase grows without preferential orientation at lower  $P_{N_2}$ , while this phase gradually grows in preferential orientation along the [111] direction when  $P_{N_2}$  becomes high.

It is clear that the phases appearing sequentially in relatively thick Cr–N films with increasing  $P_{N_2}$  during deposition are



although the  $P_{N_2}$  pressures related to these phases may vary slightly depending on the other experimental conditions.

It is worthy of note that the poorly crystallized CrN may exist even at rather low ratios of  $P_{N_2}$  in relatively thin Cr–N films, and the CrN phase formed at relatively low  $P_{N_2}$  has no preferential orientation along the [111] direction. Thus the diffraction intensity changes in Figs. 2(a) and 2(c) can be interpreted as a result of the existence of the CrN phase with vacancies.

In summary, Cr–N films were grown on Si (001) substrates by reactive magnetron sputtering. The present study shows that cubic

CrN with vacancies instead of hexagonal Cr<sub>2</sub>N may exist in Cr–N thin films produced under a low N<sub>2</sub> partial pressure.

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