Phase transformation in chromium nitride films

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The phase transformation of CrN films prepared on (100) Si substrates by cathodic arc plasma deposition was investigated at various temperatures using x-ray diffraction and stress measurements. The films were annealed in a N$_2$/H$_2$=9 reducing atmosphere over the temperature range of 300–1200 °C. X-ray diffraction results showed that an additional Cr$_2$N phase appeared both at temperatures above 1100 °C and over temperatures between 500 and 650 °C. Thermodynamics can explain the formation of Cr$_2$N at temperatures above 1100 °C but not that in the low temperature range. Nevertheless, the residual stresses in the films were determined and found to be relaxed largely over such a low temperature range. The stress states of the films were strongly correlated to the phase transformation of the films. It is concluded that the formation of Cr$_2$N at such low temperatures is mainly due to a nonthermodynamic factor—large stress relaxation occurring in the films. More experimental proof of the stress relaxation-induced phase transformation is presented. © 2003 American Vacuum Society. [DOI: 10.1116/1.1566787]

I. INTRODUCTION

Chromium nitride (CrN) films have drawn great attention in the electronics industry owing to their high hardness (1090 Hv) and low electrical resistivity (640 $\mu\Omega$ cm).$^1$ The films have also been extensively used for tribological applications because of their superior wear resistance and satisfactory oxidation resistance.$^2$ One of the most common techniques employed for preparing the films is cathodic arc plasma deposition, which is characterized by a high ion/metal ratio flux incident on the growing films.$^3$

Although much research pertains to high temperature oxidation of CrN films, only a few studies have mentioned the phase transformation of CrN into Cr$_2$N.$^4$–$^8$ Lai and Wu$^4$ pointed out that an additional Cr$_2$N phase appeared in CrN films at 1150 °C under N$_2$ and vacuum ($pO_2=1.3 \times 10^{-3}$ Pa) annealing. Hsieh et al.$^5$ also showed that a Cr$_2$N phase occurred in CrN films annealed in air over temperatures ranging from 500 to 800 °C. Héau et al.$^6$ indicated that Cr$_2$N showed up in CrN films with a Cr interlayer above 327 °C in vacuum ($pO_2=10^{-3}$ Pa). Almer et al.$^7$ mentioned that CrN would transform into Cr$_2$N at temperatures from 450 to 550 °C in Ar atmosphere and proposed that the phase transformation was due to lattice defect migration. So far, there is no unequivocal conclusion concerning the mechanism of the phase transformation in the CrN system. Because ignoring the phase transformation may cause misinterpretations of many experimental results or even misuses of the material, it is essential to look into this subject.

In our previous studies,$^8$ we reported that thermodynamics could elucidate the phase transformation above 1100 °C and proposed that a nonthermodynamic factor, i.e., the large residual stress relaxation, might induce the phase transformation over the low temperature range of 500–700 °C. In this research, more details concerning the transformation are discussed and further experimental proof is presented to validate our proposed mechanism of the phase transformation occurring especially at low temperatures.

In this research annealing has been performed over various temperatures ranging from 300 to 1200 °C in forming gas (N$_2$/H$_2$=9). Although it would cause minute oxidation, the forming gas is used because it is safer and more economical to deal with than other reducing atmospheres, such as ammonia. X-ray diffraction with an external standard is employed to examine the phase transformation of the films and the peak shift associated with changes in residual stresses. Subsequently, the stress states of the films after annealing are determined by scanning laser curvature measurements. Both as-deposited and preannealed specimens are also used to correlate the stress relaxation to the phase transformation.

II. EXPERIMENT

A. Deposition of CrN films

The substrates used for this study were p-type (100) Si wafers (Toshiba Ceramics Co., Ltd.) with a thickness of 725 $\mu$m. CrN films were directly deposited onto the substrates by cathodic arc plasma deposition with an industrial Multi-Arc physical vapor deposition system. Prior to deposition, the chamber was pumped down to a base pressure of 6.7 $\times 10^{-3}$ Pa. The bias and the current of the substrate were held at $-150$ V and 60 A under $pN_2$ of 3 Pa during deposition. The deposition time was 30 min with the corresponding thickness of the films approximately 1 $\mu$m.

B. Annealing

After deposition, the specimens were annealed under N$_2$/H$_2$=9 in a gas-tight tube furnace equipped with an oxygen sensor (15% CaO-doped ZrO$_2$) that was used to monitor...
and ensure a low oxygen level in the furnace. The flow rate was controlled at 200 sccm using a Unit 8100 mass flow controller and the soaking time was kept at 2 h through the whole research. The temperatures were monitored by S-type thermocouples. In order to elucidate the changes of residual stresses in the films with relation to the phase transformation in the low temperature range, as-deposited specimens and the specimens annealed at different temperature levels, such as 450 °C, 500 °C, and 900 °C, were selected for residual stress measurements. Moreover, several CrN specimens were pre-annealed at 900 °C in N\textsubscript{2}/H\textsubscript{2} = 9 to render a nearly complete stress relaxation, which was verified by scanning laser curvature measurements. Then the as-deposited and preannealed specimens were annealed in the same batch at 500 °C to further examine the relation between stress relaxation and the phase transformation occurring in the low temperature range.

C. Characterization

Changes in the crystal structure of the films after annealing were investigated by x-ray diffraction (MacScience MXP3, λ\textsubscript{CuKα} = 0.154 nm) operated at 40 kV and 30 mA. The collection interval and scanning rate were 0.02° (2θ mode) and 5°/min, respectively. Silicon powders (Aldrich Chemical Co., 99% purity, 325 mesh) were used as an external standard for the x-ray diffraction (XRD) measurements. To reduce errors in the peak position, the collection interval was decreased from 0.02° to 0.006° for previous CrN specimens and the standards. The residual stress measurements were performed using a scanning laser curvature method. A He–Ne laser source with a power of 7 mW and a wavelength of 632.8 nm was applied to the films. During each scanning laser curvature measurement, the laser beam traveled 100 times within a distance of 1 cm on the film surface of the laser curvature measurement. The as-deposited and preannealed specimens were annealed at 900 °C in N\textsubscript{2}/H\textsubscript{2} at 200 sccm using a Unit 8100 mass flow controller and the soaking time was kept at 2 h through the whole research. The temperatures were monitored by S-type thermocouples. In order to elucidate the changes of residual stresses in the films with relation to the phase transformation in the low temperature range, as-deposited specimens and the specimens annealed at different temperature levels, such as 450 °C, 500 °C, and 900 °C, were selected for residual stress measurements. Moreover, several CrN specimens were pre-annealed at 900 °C in N\textsubscript{2}/H\textsubscript{2} = 9 to render a nearly complete stress relaxation, which was verified by scanning laser curvature measurements. Then the as-deposited and preannealed specimens were annealed in the same batch at 500 °C to further examine the relation between stress relaxation and the phase transformation occurring in the low temperature range.

III. RESULTS AND DISCUSSION

A. XRD results of annealed CrN films

Figure 1 shows the x-ray diffraction spectra of CrN films annealed in N\textsubscript{2}/H\textsubscript{2} = 9 over the temperature range of 450 to 1200 °C. As shown in the figure, as-deposited CrN films (JCPDS No. 11-0065) exhibited a (220) preferred orientation and the CrN phase sustained over the whole temperature range. An additional Cr\textsubscript{2}N (JCPDS No. 35-0803) diffraction peak appeared over the annealing temperature range from 500 to 650 °C as well as the temperature above 1100 °C. Cr\textsubscript{2}O\textsubscript{3} (JCPDS No. 38-1479) showed up at temperatures above 650 °C. Above results are similar to our previous work although the as-deposited CrN films exhibit different preferred orientation ([220] versus [111]). It is noteworthy that CrSi\textsubscript{2} (JCPDS No. 72-1325) was also formed at temperatures above 1100 °C, which has not been investigated before.

The relative peak integrated intensities of CrN, Cr\textsubscript{2}N, Cr\textsubscript{2}O\textsubscript{3}, and CrSi\textsubscript{2} at various temperatures were further calculated using relative ratios of peak areas for CrN (220), Cr\textsubscript{2}N (111), Cr\textsubscript{2}O\textsubscript{3} (104), and CrSi\textsubscript{2} (111) diffraction peaks. The obtained results are given in Fig. 2. The minute oxidation of the films has been discussed before and this article focuses on the phase transformation of CrN into Cr\textsubscript{2}N. The temperature ranges in which Cr\textsubscript{2}N occur are similar to those of...
has been studied before, it has never been reported that CrSi₂ could be formed from the reaction of CrN with Si. Here the formation route and thermodynamic data of CrSi₂ can be written as

$$3\text{CrN} + 2\text{Si} = \text{CrSi}_2 + \text{Cr}_2\text{N} + \text{N}_2,$$  \hspace{1cm} (4)

$$\Delta G = \Delta G^0 + RT \ln(p\text{N}_2)$$

$$= (111.8 - 0.135 \times T) + RT \ln(p\text{N}_2)$$

$$= -RT \ln(p\text{N}_2)_{\text{equil}} + RT \ln(p\text{N}_2) \text{ [kJ/mol]}$$

or

$$\text{CrN} + 2\text{Si} = \text{CrSi}_2 + 1/2\text{N}_2,$$  \hspace{1cm} (5)

$$\Delta G = \Delta G^0 + RT \ln(p\text{N}_2^{1/2})$$

$$= (-9.172 - 0.058 \times T) + RT \ln(p\text{N}_2^{1/2})$$

$$= -RT \ln(p\text{N}_2^{1/2})_{\text{equil}} + RT \ln(p\text{N}_2^{1/2}) \text{ [kJ/mol]}. $$

Hence Cr₂N formed at temperatures above 1100 °C could also be due to the reaction of CrN with Si substrates as given in Eq. (4), especially when the existence of Cr₂N seems to accompany the formation of CrSi₂, as shown Fig. 2. On the other hand, Lai and Wu⁴ reported that only Cr₂N diffraction peaks occurred at 1150 °C in N₂, where the substrate was WC-30Co. Apparently, in this case the formation of Cr₂N is due to the phase transformation of CrN. Since neither possibility can be ruled out, the formation of Cr₂N above 1100 °C would stem from both the phase transformation of CrN and the reaction of CrN with Si, which could all be explained and analyzed by thermodynamics.

Surprisingly, as mentioned earlier, all the experimental data shown on the right-hand side in Fig. 3 disobey the thermodynamic prediction. In our previous paper,⁸ we have shown that diffusion-controlled mechanisms cannot be responsible for the phase transformation in the low temperature range and proposed that large stress relaxation might govern the transformation. Here we look further into this subject by carefully examining the stress factor.

C. Peak shift of CrN (220) associated with the formation of Cr₂N

If stress plays a key role in the phase transformation, peak shift of the main diffraction peak may be observed. Silicon powders were used as an external standard to calibrate the peak position of CrN (220) for the specimens. The peak shift ($\Delta 2\theta$) of CrN (220) is calculated by subtracting the reference angle of the JCPDS ($2\theta_{\text{reference}} = 63.54^\circ$) from the measured diffraction angle of the specimens ($2\theta_{\text{measured}}$). Then, the peak shift ($\Delta 2\theta$) is related to the phase transformation characterized by the relative peak intensity of Cr₂N for various annealing temperatures, as given in Fig. 4. As shown in the figure, $\Delta 2\theta$ is negative below 450 °C and its absolute value decreases with increasing temperature. $\Delta 2\theta$ reaches zero at about 500 °C and becomes positive between 500 and 650 °C, where the Cr₂N phase shows up. The trend of peak shift between 450 and 550 °C has also been observed by Almer.
et al.7 Values of \(\Delta 2\theta\) remain relatively unchanged above 650 °C, where Cr\(_2\)N also diminishes until reaching temperature above 1100 °C. Hence there is a strong correlation between the peak shift and the formation of Cr\(_2\)N in the low temperature range, which indicates that stress may play a vital role in the phase transformation.

D. Residual stresses of annealed CrN films

Because there was an indication that stress might be a key factor, the residual stresses of the films annealed at different temperatures were then further measured by a scanning laser curvature method and the corresponding residual stresses were calculated using Eq. (1). Figure 5(a) presents the measured curvatures as well as the corresponding calculated residual stresses of the as-deposited specimen and the specimens annealed at 450, 500, 550, 600, and 900 °C versus measuring points. The relation of residual stresses and the annealing temperature is also plotted as given in Fig. 5(b).

The as-deposited CrN films exhibit a compressive stress of \(-2.38\pm0.01\) GPa that is comparable to those reported from the literature \(-2.0\) to \(-8.8\) GPa.8,12–14 The residual stresses of the films annealed at various temperatures are \(-1.77\pm0.01\) (450 °C), \(-1.15\pm0.01\) (500 °C), \(0.06\pm0.01\) (550 °C), \(0.31\pm0.02\) (600 °C), and \(-0.28\pm0.02\) GPa (900 °C). Apparently, residual stresses are relaxed rapidly with increasing temperature.

The next focal point is the level of stress relaxation associated with the formation of Cr\(_2\)N. The stress relaxation is quantified by the percentage of stress relaxation \(\frac{|\sigma_{\text{annealed}} - \sigma_{\text{as-deposited}}|}{\sigma_{\text{as-deposited}}} \times 100\%\). Figure 6 shows the relative peak intensity of Cr\(_2\)N as a function of the percentage of stress relaxation. It is clearly shown that no Cr\(_2\)N could be detected below 450 °C at which the stress is only relaxed by less than 25%. Whereas at 500 °C strong Cr\(_2\)N peaks occur and stress relaxation reaches above 50%. The residual stress would be further relaxed at higher temperatures but then Cr\(_2\)N gradually diminishes and disappears above 700 °C. This can be explained by that thermodynamics start to take over since Cr\(_2\)N is not thermodynamically stable here.

E. More experimental proof of stress relaxation-induced phase transformation

As mentioned above, no Cr\(_2\)N can be detected below 450 °C while the strongest relative intensity Cr\(_2\)N shows up only at a slightly higher temperature, 500 °C. Compared to such a small temperature increment, the large difference between the stress relaxations at these two temperatures is surprising. The large stress relaxation should play a key role in the phase transformation. To further validate the proposed

![Fig. 4. Peak shift (\(\Delta 2\theta\)) of CrN (220) and the relative peak integrated intensity of Cr\(_2\)N [I\(_{\text{CrN}}\) / (I\(_{\text{CrN}}\) + I\(_{\text{Cr}2\text{N}}\)) vs annealing temperatures.](image)

![Fig. 5. (a) Measured curvatures and corresponding residual stresses of as-deposited CrN film and the films annealed at various temperatures in N\(_2\)/H\(_2\)=9 for 2 h vs measuring points. (b) Residual stresses of the CrN films as a function of annealing temperature.](image)
mechanism, another experiment was performed by using both as-deposited specimens that exhibit large residual stresses and preannealed specimens in which the stress would be mostly relaxed. As described earlier, the residual stress of the films would change from \(2\ \pm 0.01\) to \(2\ \pm 0.02\) GPa after as-deposited specimens were annealed at 900 °C. To ensure precise control of the experiment, the same CrN-deposited specimen was treated and carefully analyzed at different stages. XRD spectra of this specimen treated at different stages are given in Fig. 7. Stage I represents the as-deposited specimen that exhibited the CrN phase. Stage II shows the as-deposited specimen that was preannealed at 900 °C in \(N_2/H_2 = 9\) for 2 h. In addition to the CrN phase, \(Cr_2O_3\) was also found while no \(Cr_2N\) phase could be identified. Because CrN is much harder than \(Cr_2O_3\), the thin \(Cr_2O_3\) layer over CrN films was then carefully mechanically ground away, which is denoted as stage III. A complete oxide removal was confirmed by XRD. The underneath CrN film was examined by cross-sectional scanning electron microscopy to make sure the film remained intact. Stage IV gives the specimen that was annealed again at 500 °C in \(N_2/H_2 = 9\) for 2 h. As expected, no \(Cr_2N\) phase could be detected in this preannealed specimen. Because the two types of specimens were placed in the same annealing batch, it is noteworthy that a \(Cr_2N\) peak still showed up for the as-deposited specimen without preannealing. This demonstrates that \(Cr_2N\) cannot be formed in the low temperature range when the residual stress is fully relaxed. Hence the phase transformation occurring between 500 and 650 °C is mainly induced from the large stress relaxation during annealing.

The main reason why a small amount of \(Cr_2N\) would help relieve the stress is believed to be related to the considerably large molar volume change (\(\sim 16\%)\) when CrN transforms to \(Cr_2N\). In contrast, a relatively small molar volume change (\(< 3\%)\) during phase transformation in other rock-salt systems, like TiN and ZrN, may be the reason why similar phase transformation cannot occur when annealing is performed in the same conditions. A detailed phase transformation mechanism is worth being further investigated.

IV. CONCLUSIONS

The phase transformation of CrN has been investigated in a \(N_2/H_2 = 9\) reducing atmosphere over the temperature range from 300 to 1200 °C for 2 h using x-ray diffraction and scanning laser curvature measurements. An additional \(Cr_2N\) phase appears at temperatures above 1100 °C, as well as between 500 and 650 °C. The formation of \(Cr_2N\) at high temperatures is consistent with the thermodynamic prediction on the phase transformation of CrN and the reaction between CrN and Si. The latter reaction would also result in the formation of \(CrSi_2\).

Thermodynamics can successfully explain the phase transformation occurring at high temperature but not that in the low temperature range where \(Cr_2N\) is not thermodynamically stable. The peak shift of CrN (220) is found to be negative and its absolute value decreases with increasing temperature at such low temperatures. The residual stresses of the films measured by a scanning laser curvature technique are found to be compressive stresses and tend to be relaxed rapidly with increasing temperature. Large stress relaxation results in the formation of \(Cr_2N\) at such low temperatures. Unrelaxed as-deposited specimens and near completely relaxed annealed specimens were placed in the same annealing batch, which renders different results in the presence of \(Cr_2N\) and could further confirm that the stress relaxation governs the phase transformation. Hence the stress relaxation-induced phase transformation should be the gov-

![Fig. 6. Relative integrated intensity of \(Cr_2N\) as a function of the percentage of stress relaxation.](image)

![Fig. 7. XRD spectra of the same CrN specimen treated at different stages: (I) as-deposited, (II) preannealed at 900 °C in \(N_2/H_2 = 9\) for 2 h, (III) oxide removed for the preannealed specimen, and (IV) postannealed at 500 °C for 2 h. Unlike as-deposited specimens, a \(Cr_2N\) phase would not appear in the relaxed preannealed specimen.](image)
ering mechanism of forming Cr$_2$N in the low temperature range.

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