Degradation of CrN films at high temperature under controlled atmosphere

Fu-Hsing Lu, a, Hong-Ying Chen, and Chih-Hung Hung
Department of Materials Engineering, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan

(Received 15 May 2002; accepted 18 February 2003; published 11 April 2003)

The degradation of CrN films was investigated over temperatures of 400–1200 °C in air, nitrogen, and forming gas (N₂/H₂ = 9) by analyzing changes in color and appearance, as well as microstructures. The degradation mainly included color changes and cracks occurring on the film surface. The color change resulting from low-temperature/short-time annealing was due to the formation of an additional Cr₂N phase, as well as a thin oxide overlayer. The color change appearing at higher temperatures/longer times stemmed from the formation of a thicker Cr₂O₃ layer, whose content depended on the pN₂/pO₂ ratio in the atmosphere. The driving force of the oxidation was the Gibbs free-energy change for CrN and Cr₂O₃. Cracks that showed up at relatively high temperatures were attributed to the large thermal mismatch between the CrN film and Cr₂O₃ overlayer. The thermal stresses were calculated and discussed. The degradation diagrams were generated based on the above analyzed results. © 2003 American Vacuum Society.

I. INTRODUCTION

Chromium nitride (CrN) films have drawn great attention for tribological applications owing to their satisfactory oxidation resistance, as well as corrosion and wear resistance. Because of low resistivity, the films may also be applied within the electronics industry. The oxidation of CrN films has been extensively studied in dry oxygen, nitrogen, argon, and vacuum. Oxidation is one of the main causes leading to degradation in the films. As pointed out in our previous paper, only a rather small range of oxygen partial pressures (mostly pO₂ = 1 × 10⁻⁵ atm, except in vacuum) has been considered in the above literature. So far, there is a lack of systematic studies on the degradation of thin films annealed in different atmospheres. Besides, annealing is an important tool to understand the microstructure of the films because the microstructure may change with temperature, as well as with atmosphere. Moreover, the films may also be used at various temperatures and in diverse atmospheres; hence it is essential to look into how the films react under different annealing conditions.

In our previous study, we reported the results on the degradation of TiN films at high temperature under controlled atmosphere. Oxidation and fracture induced by a large thermal mismatch between the film and the substrate are primary sources of degradation in TiN. This research focuses on the degradation of CrN films after annealing in the controlled atmosphere. The degradation in CrN may behave differently because phase transformation is involved, as well as oxidation and thermal stress. A wide temperature range of 400–1200 °C was selected for annealing. Air, N₂, and forming gas (N₂/H₂ = 9) were chosen because drastically different pN₂/pO₂ ratios in the atmosphere are suitable for comparison. Changes in appearance and resultant microstructures after annealing were analyzed. The degradation diagrams were generated according to the analyzed results.

II. EXPERIMENT

CrN films were directly deposited onto Si substrates by cathodic arc plasma deposition. The deposition parameters were as follows: Cr metal cathode, substrate bias −150 V, current 60 A, pN₂ 3 Pa, and deposition time 30 min. The thickness of the film was about 1 μm, determined by cross-sectional scanning electron microscopy.

Annealing was performed over temperatures between 400 and 1200 °C in a gas-tight tube furnace equipped with a zirconia (15 mol % CaO-doped) O₂ sensor. The flowing gases contained air, pure nitrogen (N₂ = 99.999%), and forming gas [N₂/H₂ = 9; H₂ = (10 ± 0.2)%], which possess similar pN₂, but drastically different pO₂. The value of pO₂ is 0.21 atm in air, ~10⁻⁵ atm in “pure” nitrogen, and a function of temperature in N₂/H₂ = 9 (e.g., ~10⁻₂⁵ atm at 700 °C, ~10⁻²⁰ atm at 900 °C, and ~10⁻¹⁶ atm at 1100 °C). The flow rate was controlled at 200 sccm by using a Unit 8100 mass flow controller. The pressure in the furnace was kept at about 1 atm. The ramping rate was about 5 °C/min, and the soaking time varied from 2 to 12 h.

After annealing, the films were first inspected under an optical microscope. The color of the film was also further analyzed by visual spectroscopy (MacBeth, Color Eye 3000). The crystal structure of the film was determined by a MacScience MXP3 x-ray diffractometer operated at 40 kV and 30 mA (λCu,Kα = 0.154 nm). A Physical Electronics (ESCA PHI 1600) x-ray photoelectron spectrometer (XPS) with a Mg Kα source in the energy of 1253.6 eV was used to analyze changes in the surface chemical state of the film. The Cr-2p, N-1s, and O-1s high-resolution spectra covering 20 eV were collected and calibrated with respect to the C-1s peak at 284.8 eV from the adventitious hydrocarbon con-

---

Author to whom correspondence should be addressed; electronic mail: fhlu@dragon.nchu.edu.tw

[DOI: 10.1116/1.1566784]
tamination. Each XPS spectrum was fitted using a nonlinear least-squares fit with a Gaussian/Lorentian (G/L mixing ratio = 0.3) peak shape. The morphology of the film after annealing was carefully examined by a JEOL JSM-5400 scanning electron microscope operated at 15 kV.

III. RESULTS AND DISCUSSION

After annealing, the color of CrN films changed from originally silver-gray to golden, purple, and green, depending on the annealing temperature, time, and atmosphere. Cracks appeared on the film surface at relatively high temperatures under all atmospheres. Color changes and cracks are two main types of degradation occurring in the films. Degradation diagrams were then generated by plotting the regions of color changes and cracks occurring at various annealing temperatures and times under controlled atmosphere; see Figs. 1(a) air, 1(b) N₂, and 1(c) N₂/H₂ = 9.

A. Color change

Figures 1(a)–1(c) depict two types of color changes, denoted as regions I and II. In general, region I (∆) represents the films that turned golden, and region II (+) shows films that became purple. At higher temperatures, the films turned green, and cracks could then be observed on the film surface, denoted as ×. The symbol ○ represents no color change. As shown in the figures, the boundary line between the region of no color change ○ and region I of color changes (∆) was located at similar temperatures and times under all atmospheres. However, the boundary line between regions I (∆) and II (+) shifted to higher temperatures for N₂, and N₂/H₂ = 9 compared to that for air. This means that the color change of films in N₂ and N₂/H₂ = 9 was not as severe as that in air where the pO₂/pN₂ ratio is relatively high. The occurrence of cracks on the film surface behaved in a slightly different manner in various atmospheres as will be discussed later.

To characterize the causes of color changes, x-ray diffraction (XRD) was first employed to analyze changes in the crystal structure for each annealed specimen. XRD results of the as-deposited films and the films annealed at various temperatures and times for different atmosphere are given in Figs. 2(a) air, 2(b) N₂, and 2(c) N₂/H₂ = 9. Only some of the results are given for comparison. The data were selected according to the different types of degradation shown in Figs. 1(a)–1(c). It is clearly shown in all XRD results that only the original CrN phase (JCPDS 11-0065) appeared if there was no color change occurring on the film. For region I of color changes given in Figs. 1(a)–1(c), the corresponding XRD results show an additional β-Cr₂N phase (JCPDS 35-0803). The reaction of the phase transformation can be written as follows:

\[
2\text{CrN} = \text{Cr}_2\text{N} + \frac{1}{2}\text{N}_2.
\]

The Gibbs free-energy change of the reaction \(\Delta G\) and the standard Gibbs free-energy change \(\Delta G^0\) are given below by summarizing the thermodynamic data from the literature: 25

**Fig. 1.** Degradation diagrams of CrN films annealed at various temperatures/times for (a) air, (b) N₂, and (c) N₂/H₂ = 9. The symbol ○ represents no color change, ∆ indicates color-change region I (golden), + indicates color-change region II (purple), and × indicates a green color change plus cracks occurring in the film.
\[
\Delta G = \Delta G^0 + RT \ln(pN_2^{1/2}) - (0.107 \times T) + RT \ln(pN_2^{1/2}) \text{ [kJ/mol].}
\]

From our previous analyses, the CrN phase is thermodynamically stable only above 1010°C vs 1084°C calculated from above new data in nitrogen (pN₂ = 1 atm). Hence the formation of CrN in region I mainly resulted from the additional Cr₂N phase, the color change should only be influenced by pN₂ and be independent of pO₂, according to Eq. (1). This means that the left boundary line defining region I of color changes should be located at a similar temperature-time range for all atmospheres investigated. The experimental results are consistent with this prediction. Hence the golden color should mainly be due to the formation of Cr₂N as well as a thin oxide overlayer which was identified by XPS but was not thick enough to be detected by XRD. Typical Cr-2p and O-1s high-resolution spectra of CrN films annealed in region I, at \( \sim 500°C \) for 2 h, are given in Figs. 3(a) and 3(b). The binding energies (BE) of Cr-2p\(_{3/2}\) = 576.2 eV, Cr-2p\(_{1/2}\) = 585.9 eV (\( \Delta \text{BE} = 9.7 \text{ eV} \)), and O-1s = 530.0 eV in all atmospheres can be characterized as Cr₂O₃ using the data reported from the literature. The peak energies at 574.6 eV (Cr-2p\(_{3/2}\)) and 584.3 eV (Cr-2p\(_{1/2}\)) with \( \Delta \text{BE} = 9.7 \text{ eV} \) in Cr-2p spectra for as-deposited specimens can be identified as CrN. Because Cr₂O₃ could not be detected from the XRD results, the surface Cr₂O₃ identified from XPS under such annealing conditions was rather thin.

At higher annealing temperatures or longer times located in region II of color changes, XRD results show that a crystalline Cr₂O₃ phase is formed. Clearly, the purple color in the region is due to the formation of a thicker Cr₂O₃ layer. The oxidation of CrN could then be formulated by

\[
2\text{CrN} + \frac{1}{2}\text{O}_2 = \text{Cr}_2\text{O}_3 + \text{N}_2.
\]

The Gibbs free-energy change is given as

\[
\Delta G = \Delta G^0 + RT \ln \left( \frac{pN_2}{pO_2^{3/2}} \right) = (-904.474 + 0.107 \times T) + RT \ln \left( \frac{pN_2}{pO_2^{3/2}} \right) \text{[kJ/mol].}
\]

Although the oxidation of CrN may also contribute to the formation of Cr₂O₃, the amount of the phase is so small that the contribution can be nearly ignored. As mentioned above, if region II of color changes is mainly due to the formation of Cr₂O₃, then the left boundary line defining region II should be greatly influenced by the pN₂/pO₂ ratio in the atmosphere, as predicted by Eq. (4). As given in Figs. 2(a)–2(c), this boundary line shifted toward higher temperature for a fixed annealing time. The degree of the shift followed the sequence: N₂/H₂ > N₂ > air. That sequence indicates that oxidation would be retarded in an atmosphere with relatively high pN₂/pO₂ ratios. Again, the experimental results are consistent with the thermodynamic prediction.
B. Cracks

As mentioned earlier, cracks were observed on the film surfaces above about 800 °C under all atmospheres. The cracks were present in the Cr₂O₃ overlayer but did not penetrate through the CrN films. This is shown in Figs. 4(a) and 4(b), which display the morphology of the films annealed at 900 °C in N₂/H₂ for 2 h before and after part of the surface oxide layer was ground away. All the films with cracks turned green and were constituted mainly of Cr₂O₃ and CrN phases, as shown in the previous XRD results. To pinpoint the origin of cracks, the thermal stresses in Cr₂O₃ and CrN are calculated by using a bilayer model, which has also been discussed in our previous study. Consider Cr₂O₃/CrN as a laminate structure. The unrelaxed thermal stress in Cr₂O₃, \( \sigma_{\text{Cr}_2\text{O}_3} \), resulting from the thermal mismatch between the two materials could be written as

\[
\sigma_{\text{Cr}_2\text{O}_3} = \frac{(\alpha_{\text{Cr}_2\text{O}_3} - \alpha_{\text{CrN}})\Delta T}{\frac{\nu_{\text{Cr}_2\text{O}_3} - 1}{E_{\text{Cr}_2\text{O}_3}} + \frac{h_{\text{Cr}_2\text{O}_3}}{E_{\text{Cr}_2\text{O}_3}} \times \frac{\nu_{\text{CrN}} - 1}{E_{\text{CrN}}}},
\]

with \( \alpha \) the thermal expansion coefficient \( [\alpha_{\text{Cr}_2\text{O}_3} = 9.55 \times 10^{-6} \text{ K}^{-1}, \alpha_{\text{CrN}} = 2.3 \times 10^{-6} \text{ K}^{-1} \text{ (Ref. 30)}] \), \( \Delta T \) the temperature change between annealing temperature and room temperature, \( \nu \) the Poisson ratio \( [\nu_{\text{Cr}_2\text{O}_3} = 0.29, \nu_{\text{CrN}} = 0.199 \text{ (Ref. 32)}] \), \( E \) the Young’s modulus \( [E_{\text{Cr}_2\text{O}_3} = 280 \text{ GPa}, E_{\text{CrN}} = 452 \text{ GPa (Ref. 32)}] \), and \( h \) the thickness of the material. Consider annealing at 900 °C in N₂/H₂ = 9, the calculated unrelaxed thermal stress, \( \sigma_{\text{Cr}_2\text{O}_3} \), is about 2.5 GPa, with \( h_{\text{Cr}_2\text{O}_3} \approx 0.1 \mu\text{m} \) and \( h_{\text{CrN}} \approx 1 \mu\text{m} \) as determined by cross-sectional scanning electron microscopy.

The unrelaxed thermal stress in CrN, \( \sigma_{\text{CrN}} \), resulting from the mismatch between CrN films and Si substrates is

\[
\sigma_{\text{CrN}} = \frac{(\alpha_{\text{CrN}} - \alpha_{\text{Si}})\Delta T}{\frac{\nu_{\text{CrN}} - 1}{E_{\text{CrN}}} + \frac{h_{\text{CrN}}}{E_{\text{CrN}}} \times \frac{\nu_{\text{Si}} - 1}{E_{\text{Si}}}},
\]

Fig. 3. X-ray photoelectron spectroscopy results of CrN films annealed at 500 °C in different atmospheres for (a) Cr-2p and (b) O-1s spectra.

Fig. 4. Morphology of CrN films annealed at 900 °C in N₂/H₂ = 9 for 2 h (a) before and (b) after part of the surface oxide layer was ground away. It is clearly shown that cracks appear only in the Cr₂O₃ overlayer and do not penetrate through the CrN film.
with $\alpha_{Si}=2.45 \times 10^{-6}$ K$^{-1}$, $\nu_{Si}=0.279$, $E_{Si}=130.2$ GPa, and $h_{Si}=725$ μm. The calculated thermal stress in CrN is about 0.074 GPa using the same above annealing conditions. Apparently, compared to an extremely large thermal mismatch between CrN and Cr$_2$O$_3$ ($\sim 320\%$), such a small thermal mismatch between CrN and Si ($\sim 7\%$) would result in negligible thermal stresses in both CrN and Si. In contrast, as long as Cr$_2$O$_3$ shows up, large thermal stress starts to build up and would cause the fracture of the films. By measuring the critical thickness of the oxide, at which cracks begin to occur, and controlling the annealing parameters, the fracture strength of the oxide could then be determined by using the bilayer model, as given in Eq. (5). In our experiments, the observed minimum temperature at which cracks occur is 800 °C. Because the oxide layer is rather small, the second term in the denominator of Eq. (5) can be neglected. The minimum thermal stress $\sigma_{Cr_2O_3}$ that would induce cracks is determined to be 2.0 GPa, which can be considered as the fracture strength of Cr$_2$O$_3$ films. So far, there are no fracture strength data available in the literature for Cr$_2$O$_3$. The obtained value is quite reasonable because the fracture strength of commercial ceramics in the range of $E/100-E/1000$ or less ($E_{Cr_2O_3}=280$ GPa) is typically observed. 28

IV. CONCLUSIONS

The degradation of CrN films annealed in the controlled $p_{N_2}$ and $p_{O_2}$ atmosphere mainly includes color changes and cracks occurring on the film surface. The color change appearing in the low-temperature range is the formation of an additional Cr$_2$N phase, together with a very thin oxide layer over the nitrides. The color change occurring at higher temperatures and longer annealing times stems from the thicker Cr$_2$O$_3$ phase. Cracks occur in Cr$_2$O$_3$ overlayers at relatively high temperatures for all atmospheres. The degradation diagrams are generated accordingly by distinguishing the regions of color changes and cracks occurring at various annealing temperatures and times.

The formation of an additional Cr$_2$N phase results from the large stress relaxation in the film. The formation of Cr$_2$O$_3$, whose content depends on the $p_{N_2}/p_{O_2}$ ratio in the atmosphere, can be analyzed by thermodynamics. The driving force of the oxidation is the Gibbs free-energy change for CrN and Cr$_2$O$_3$. Cracks on the film surface are mainly due to the large thermal mismatch between CrN and Cr$_2$O$_3$. The fracture strength of Cr$_2$O$_3$ can be deduced from the bilayer model by determining the annealing conditions where cracks begin to occur.

ACKNOWLEDGMENTS

This work is sponsored by the National Science Council of the R.O.C. (Taiwan) under Grant No. NSC 90-2216-E-005-018. The authors also appreciate Surftech Corporation, Taiwan, for preparing the CrN films.