JOURNAL OF MATERIALS SCIENCE 33 (1998) 3251–3254

Synthesis and properties of CeN thin films deposited by arc ion plating

S. Q. XIAO, K. TSUZUKI, H. SUGIMURA, O. TAKAI
Department of Materials Processing Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan
E-mail: takai@otakai.numse.nagoya-u.ac.jp

Cerium nitride films were deposited by ion plating in an electron-beam sustained Ce arc discharge in a nitrogen atmosphere. The crystal structure was strongly affected by the arc discharge current and the substrate temperature. The lattice spacing of CeN film is 0.5020 nm with a density of 7.82 g cm^{-3}. This film showed a paramagnetic property at 10 K in a magnetic field of 20 kOe. The Knoop hardness for CeN film is over 1600. The electrical resistivity was 4.6×10^{-4} Ω cm with p-type conductivity. The carrier concentration of the CeN film increased after exposure to the air, which suggested that the valence of Ce in CeN is probably 4+. © *1998 Kluwer Academic Publishers*

1. Introduction

CeN was studied mainly in the 1960s and 1970s [1–5]. Gambino and Luomo [1] developed a method called reactive melting in nitrogen gas to form CeN. The arc was sustained for only 1 min in nitrogen gas. Introduction of Ar gas at intervals was needed to prevent the arc from extinguishing and to keep the metal in a melting state in the nitrogen gas. The sample was formed by a few such cycles of melting and nitriding. Occlusion of rare-earth metal was found in the grain boundary of the CeN crystal. Dell and Hensley [2] synthesized a CeN sample by first forming cerium hydride with a small piece of Ce reacting with H_2 at 673 K and then converting the hydride to nitride by heating the sample to 1073 K in nitrogen gas. The sample had 90% of the nitrogen required for stoichiometric CeN. Few reports can be found in recent years owing to the instability of the sample in the air in spite of some interesting properties, such as p-type conductivity. However, the problem of instability can be solved simply now by proper coating of protective layer.

The aim of this work is to synthesize CeN films and to characterize them in terms of crystal structure, electrical and mechanical properties. The chemical stability of films in an ambient atmosphere was investigated in detail.

2. Experimental procedure

Fig. 1 shows a schematic diagram of the equipment employed in this study. The chamber (450 mm in diameter, and 450 mm in height) was evacuated to 10^{-5} Pa by rotary and oil diffusion pumps before deposition. The borosilicate glass and Si substrates were mounted on a floating rotation system to achieve uniform thickness. The substrate temperature was altered from room temperature to 673 K.The substrates were cleaned by Ar radio frequency plasma for 15 min at a pressure of 8.0×10^{-2} Pa before deposition. Nitrogen was introduced into the chamber to 7.0×10^{-2} Pa together with helium gas at the partial pressure of 1.0×10^{-2} Pa. The addition of helium gas improved the stoichiometry of the films and led to stability of the films, probably because of the high energy of helium gas in a metastable state, which excited nitrogen to states with higher reactivity [6].

A Ce (purity, 99.9%) chunk in a water-cooled copper crucible was evaporated with an electron-beam (EB) gun; an electrode made of molybdenum for arc discharge was positioned 30 mm over the edge of the melted Ce pool and a positive direct-current voltage of 25 V was applied to the electrode. An arc discharge of 20–60 A was established between the source and the electrode by changing the EB power. An optical multichannel analysing system with charge-coupled device and optical fibres was used for the optical emission measurement of the plasma. The position of the measurement was in the centre of the space between the crucible and the substrate.

A small-angle (0–10°) X-ray diffractometer (Rigaku; Cu $K\alpha$) made it possible to study the crystal structure of thin films. The electrical properties were investigated by the van der Pauw method. The density of the films was calculated by dividing the mass gain of the samples by the film volume. The magnetic properties were investigated by means of a vibrating-sample magnetometer down to 10 K in the magnetic field of 20 kOe. The hardness was measured with an ultramicro-hardness tester. The compositions and binding states of the films were studied by X-ray photoemission spectroscopy (XPS).

0022–2461 © *1998 Kluwer Academic Publishers*

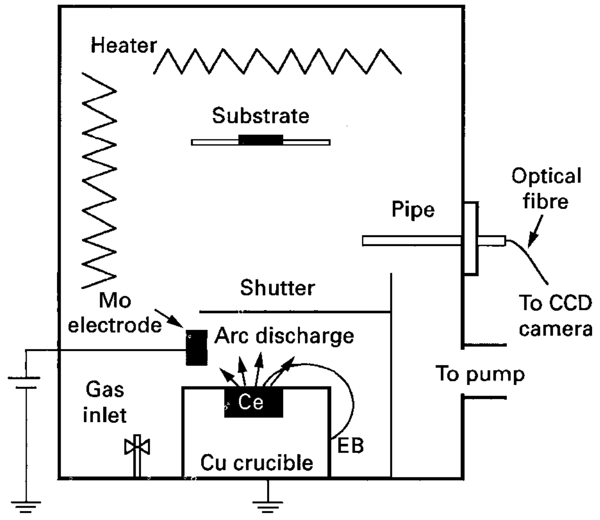

Figure 1 The sketch diagram of the apparatus utilized in the experiment, CCD, charge-coupled device, EB, electron beam.

3. Results and discussion

3.1. CeN film formation process

Cathodic arc evaporation is widely used to synthesize new ceramics, such as TiN and TiC, and the mechanism of this arc discharge has been well studied [7]. The ionization degree of nitrogen gas is very high owing to the charge transfer from the metal ion to the nitrogen gas. On the other hand, the EB-evaporated Ce vapour arc discharge in this study exhibited a quite different feature. Fig. 2 shows the optical emission spectra in the range 330–400 nm. Emission peaks from three species (N_2, Ce and Ce^+) in this range were analysed. The N_2 second positive transitions (0, 0), (1, 2) and (0, 1) were observed clearly when $I_a = 20$ A and the emission intensity became lower with increasing arc current, I_a. When I_a reached 60 A, these peaks were very low. Ce and Ce^+ indicated another tendency. Emission peaks from Ce and Ce^+ increased continuously with increasing arc current. From the results of the crystal structure and XPS analysis described below, the stoichiometric composition was achieved only at $I_a = 60$ A. Ce^+ was considered to play an important role in the formation of the CeN film.

This was proved by applying a positive bias voltage of +100 V to the substrates to prevent positive ions from bombarding the substrates; a thin Ce film with about 8 at% N was found on the conductive substrate, whereas a thick CeN film was formed on the glass insulating substrate in the same substrate holder. This indicated that CeN was hard to form without bombardment of Ce^+. It was supposed that reaction of Ce with nitrogen takes place by the following processes:

(a) N_2 molecules were adsorbed on the substrate surface.

(b) Ce^+ obtained high energy from the potential hump in the arc discharge as described by Davis and Miller [8].

(c) The impinging Ce^+ ions bombarded the N_2 molecule attached to the substrate surface and made the N_2 molecule decompose into atomic nitrogen.

(d) Ce^+ ions obtained one electron from the substrate, became neutral atom and then reacted with the N atoms. CeN was formed.

3.2. Crystal structure

3.2.1. Effect of arc discharge current

The room-temperature phase of metallic cerium has a face-centred cubic lattice with a unit cell size only 2.25% larger than that of CeN. As the nitriding process proceeded, a change in the lattice spacing was observed. The variation in X-ray diffraction patterns under different arc currents, I_a, is shown in Fig. 3. When $I_a = 20$ A, besides the Ce 1 1 1 peak, a broad peak of CeO_2 1 1 1 was also observed, which originated from the oxidation of Ce in the air. When I_a increased to 40 A, the CeO_2 1 1 1 peak intensity decreased, whereas the initial Ce 1 1 1 peak became

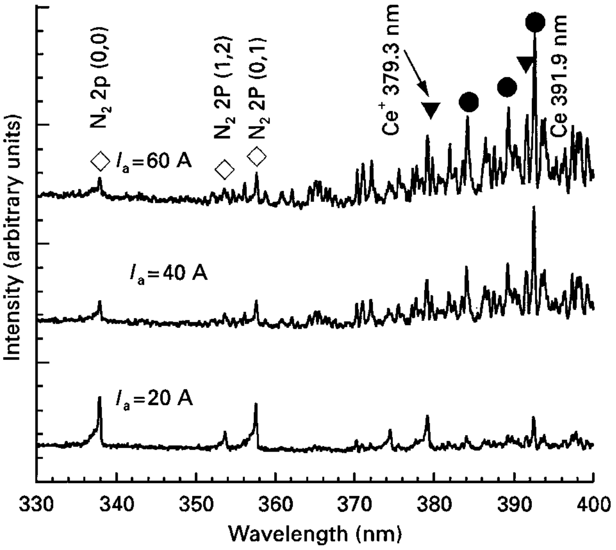

Figure 2 Optical emission spectra at different arc discharge currents, I_a. (●), Ce atom; (▼), Ce^+ ion; (◇), N_2 molecule.

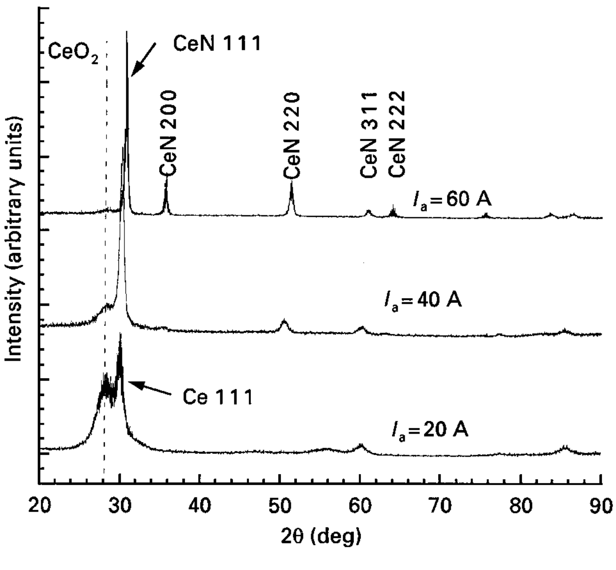

Figure 3 Crystal structure change as a function of arc discharge current, I_a.

stronger and shifted to larger angles, approaching the CeN 1 1 1 peak. Stoichiometric CeN was formed only when the arc current reached 60 A or more; the initial Ce 1 1 1 peak was replaced by a strong CeN 1 1 1 peak. As I_a was increased from 20 to 40 to 60 A, the lattice spacing d decreased from 0.5948 to 0.5916 to 0.5020 nm. This corresponded to a unit-cell volume decrease of 2.7%. Quantitative analysis of the CeN film by XPS confirmed an increase in nitrogen content in the film with increasing current. The films fabricated at $I_a = 60$ A showed a stoichiometric composition. We could see the change in crystal structure from face-centred cubic Ce metal to CeN with NaCl structure from the contraction of lattice spacing. The full width at half-maximum (FWHM) of the peaks from Ce 1 1 1 to CeN 1 1 1 decreased from 0.800° to 0.517° to 0.447°; the bombardment of Ce ions on the film surface might contribute much to the CeN crystal growth.

3.2.2. *Substrate temperature*

The crystal structures of CeN films were also sensitive to the substrate temperature (shown in Fig. 4). It was found that there was an optimal temperature range for CeN film growth. When the substrate was heated to 373 K or not heated deliberately, the intensities of the peaks were low and the intensity of the CeN 2 0 0 peak was stronger than that of the CeN peak 1 1 1, which was also a sign of excessive Ce metal in the film, because the Ce 1 0 1 peak appeared at the same position as the CeN 2 0 0 peak and was added to the CeN 2 0 0 peak. When the substrate temperature reached 673 K, the crystal structure deteriorated again. This was because CeN formation is an exothermic reaction, from a thermodynamic point of view; 673 K might be too high a temperature for this reaction. The optimal temperature range was between 473 and 573 K in our conditions. The films showed strong 1 1 1 orientation in this range. Compared with 1073 K [2], the temperature for thermal reaction between N_2 and Ce metal, the temperature in our study was very low owing to enhanced reactivity of Ce vapour and nitrogen by arc discharge.

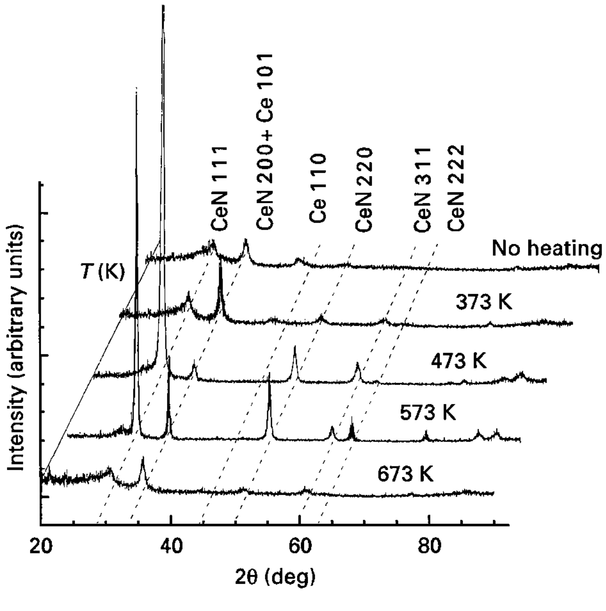

Figure 4 The influence of temperature on the crystal structure.

3.3. Properties

3.3.1. *Electrical and magnetic properties*

The electronic structure of CeN was investigated by Pickett and Klein [9] and Brooks [10]. Calculations showed a wide band of 4f states located just above E_F and confirmed the existence of considerable f–f overlap in CeN. No band gap was observed in the dispersion curve. Dell and Hensley [2] reported that the resistivity of their CeN_x sample was 2.1×10^{-5} Ω cm. However, their samples were non-stoichiometric with nitrogen deficiency, which inevitably affected the electrical properties. We obtained a different value using the stoichiometric sample. The resistivity was 4.57×10^{-4} Ω cm, the carrier concentration 1.49×10^{20} cm^{-3} and the mobility 92.1 cm^2 V s^{-1}. The conductivity was p type. No oxidation of the sample took place instantly after exposure to the air, especially when the films had a stoichiometric composition. After exposure to the air for 1 h, there was little change in the crystal structure, resistivity and carrier concentration. Our measurement was performed immediately after the samples were taken out of the chamber. Therefore it is reasonable to think that surface oxidation had little effect on our electrical resistivity results.

The magnetic measurement proved that CeN showed a paramagnetic property at 10 K. The applied magnetic field was 20 kOe.

3.3.2. *Hardness and density*

The lattice energy of LaN and ScN was near that of TiN [11]. CeN is expected to be a hard material because of the similarity in crystal structure (NaCl type) and electronic configuration to LaN and ScN. No data on mechanical properties have been reported yet. The thicknesses of our samples were less than 1 μm. The ultramicrohardnesses were 503 for the CeN film, and 450 for Si. CeN proved to be harder than Si. The knoop hardness of the Si wafer was about 1500 and that of the CeN film might be over 1600.

The density of stoichiometric CeN was 7.82 g cm^{-3}, which was near 8.00 g cm^{-3}, the value estimated by theoretical calculation from the lattice spacing obtained from the X-ray diffraction results.

3.3.3. *Stability*

The negative enthalpy of formation for CeN is reported to be 78 kcal (g-atom)$^{-1}$ [12], lower than that of TiN (80 kcal (g-atom)$^{-1}$). The oxidation process of the CeN film in the air at room temperature was investigated using X-ray diffraction and the van der Pauw method in our study. Fig. 5 shows the change in X-ray diffraction patterns as a function of the exposure time. After exposure to the air, for 4 h, no obvious change in the intensity and FHWM was observed except that the CeO_2 peak became a little stronger.

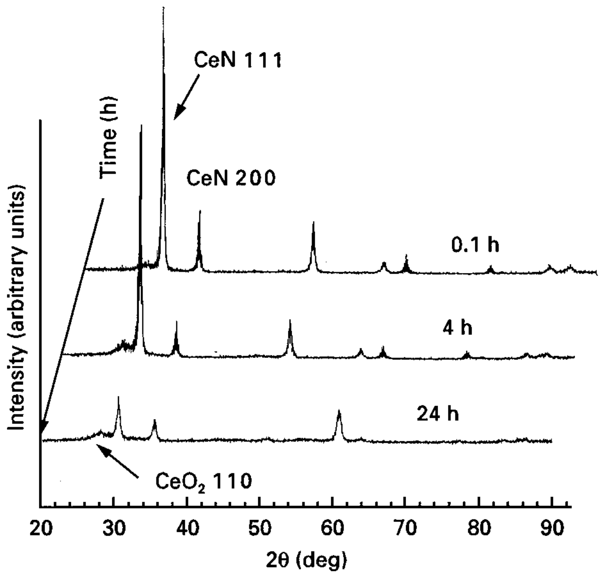

Figure 5 X-ray diffraction patterns change during the oxidation process of CeN in air.

The intensity of the CeN 1 1 1 peak in the same sample decreased significantly after exposure for 24 h, which indicated that the CeN lattice was preserved, but in much less order. After 15 days, the CeN peaks disappeared and this film changed to a CeO_2-like substance.

When the sample was put in the ambient atmosphere, the carrier concentration increased for the first few hours and then decreased as shown in Fig. 6. Because the mobility underwent a constant increase, the electrical resistivity increased continuously. Oxidation of nitride films generally makes the carrier concentration decrease because of the formation of insulating oxide. The anomalous increase in the carrier concentration due to oxidation may provide information on the mechanism of the p-type conductive property in CeN. It was believed that the increase in Ce^{4+} concentration accounted for the increase in the carrier concentration, because the oxidation was the most probable reaction in the air. To explain this phenomenon, the electronic configuration has to be considered. Ce has a $6s^2 4f^2$ outer shell; there is a tendency for Ce to lose the two 4f electrons (Ce^{4+}) rather than one (Ce^{3+}), which leads to an energy decrease (ΔE_1, for example) in the whole system. This is also the reason why CeO_2 is much more stable than Ce_2O_3. For CeN, three electrons from Ce are generally needed to form the bond with N. When one more electron from the 4f orbit joins the bond, this electron has to enter the antibonding orbital in the CeN molecular orbital and the energy will increase (ΔE_2 for example). If $\Delta E_2 < \Delta E_1$, Ce will prefer the Ce^{4+} to the Ce^{3+} state in CeN and one hole will be left in the 4f orbital. This might be the origin of the p-type conductivity of CeN. XPS analysis also showed that the Ce^{4+} component did exist in the sample. Another explanation for the p-type conductivity is that, as Ce combines with oxygen, the nitrogen became excessive over Ce in the film, which also led to p-type conductivity. After 4 h (Fig. 6) had passed, the CeO_2-like insulator structure began to form and caused the decrease in carrier concentration.

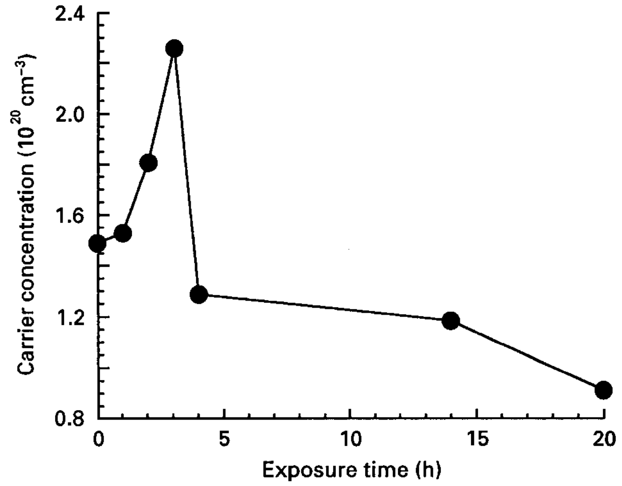

Figure 6 Anomalous increase in carrier concentration of the CeN film after exposure to air.

4. Conclusion

Stoichiometric CeN was obtained at an arc current, I_a, of 60 A in the substrate temperature range 473–573 K. Optical emission from the discharge revealed that the arc discharge was localized in Ce vapour; Ce was highly ionized; however, the excited state of nitrogen was low. Ce^+ was assumed to play an important role in the formation of CeN film. The density of the film with stoichiometric composition was 7.8 g cm^{-3}, close to the theoretically calculated value. The Knoop hardness for the CeN film is over 1600. The resistivity was 4.57×10^{-4} Ω cm. The increase in carrier concentration in the film in an ambient condition suggested that the valence of Ce in CeN may be over 3 +, probably 4 +, which led to p-type conductivity. The mobility of the carrier was fairly high; it might find applications in non-electrical input devices or thermoelectric devices.

References

1. R. J. GAMBINO and J. J. CUOMO, *J. Electrochem. Soc.* **113** (1966) 401.
2. K. D. O. DELL and E. B. HENSLEY, *J. Phys. Chem.* **33** (1972) 443.
3. N. SCLAR, *J. Applied Phys.* **35** (1964) 1534.
4. M. R. MORMAN and D. D. KOELLING, *Phys. Rev.* B **31** (1984) 6251.
5. U. VON ESSEN and W. Z. KLEMM, *Anorg. Allg. Chem.* **317** (1962) 25.
6. S. DE BENEDICTIS and G. DILECCE, *Plasma Sources Sci. Technol.* **4** (1995) 212.
7. M. SAKAKI and T. SAKAKIBARA, *IEEE Trans. Plasma Sci.* **22** (1994) 1049.
8. W. D. DAVIS and H. C. MILLER, J. Appl. Phys. **40** (1969) 2212.
9. W. E. PICKETT and B. M. KLEIN, J. Less-Commun. Metals **93** (1983) 219.
10. M. S. S. BROOKS, *J. Magn. Magn. Mater.* **47–48** (1985) 260.
11. C. W. ROBERT, in "Handbook of chemistry and physics" (CRC Press, Boca Raton Florida, 59th Edn, 1978) p. D101.
12. C. N. R. RAO, in "Chemistry of advance materials" (Blackwell Scientific, Oxford, 1990) p. 169.

Received 9 July 1997
and accepted 2 April 1998