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Preparation and characterization of Ni-C composite films

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Ni-C composite films were prepared using a codeposition method, their structure and electrical properties were investigated. Depending on experimental conditions, two typical structures are found for as-deposited Ni-C films: i) amorphous Ni-C alloy film; ii) granular film with Ni_3C granules and inter-granule amorphous carbon. The amorphous Ni-C films show ohmic conduction behaviour with very high resistivity. On the other hand, granular films with high carbon content show semiconductive characteristics. The electrical property and conduction behaviour are correlated with the film structure. Besides, the crystallization behaviour of the amorphous Ni-C film was also studied. *© 2001 Kluwer Academic Publishers*

1. Introduction

Nanostructured composite films have attracted both scientific and technological interests in recent years because of their size-dependent novel properties, and the fact that their properties can be controlled by adjusting the deposition parameters [1]. Such films are generally prepared by sputtering, laser ablation of composite material targets, or by reactive sputtering of metal targets, with their structures covering the combinations of metal-insulator and metal-semiconductor [2, 3]. In our previous work [4], we have reported the formation of Ni_3C nanocrystallites in codeposited Ni-C films, in which amorphous carbon was also incorporated. Amorphous carbon films, due to their hardness and chemical inertness, are often used as protective coatings against friction and corrosion [5–7]. In addition, the conductivity of amorphous carbon films depends strongly on the bonding state of carbon, the films varied from insulators to semiconductors and even to conductors depending on the deposition method and conditions [8]. Therefore, nanostructure composite films combining metal and amorphous carbon may also yield novel mechanical and electrical properties. In the present work, the structure and electrical properties of Ni-C composite films were investigated.

2. Experimental

A dual-source deposition system was used to prepare the Ni-C composite films, which includes a Kaufman ion source [9] used for ion beam sputtering deposition of Ni, and a compact electron cyclotron resonance (ECR) plasma source for chemical vapor deposition (CVD) of carbon. Plasma CVD has been widely used for the deposition of carbon films such as diamond, diamond-like and a-C : H films [10–12]. During deposition, the Kaufman ion source was operated to produce an argon ion beam directing to a Ni target (99.99%) with an energy of 2 keV and a beam current of 20 mA. The reaction gases supplied to the ECR plasma source were premixed methane (CH_4) and hydrogen (H_2) gases with their flow rate controlled by mass flow controllers. The power supplied to the source was fixed to 245 W. The substrates used were freshly cleaved rock salt (NaCl) and glass slides respectively for structure analysis and property measurements. Nickel and carbon were codeposited onto these substrates by simultaneously operating the two sources. Before depositions, the system was evacuated to a base pressure of less than 6×10^{-5} Pa. The structure of the films were characterized by transmission electron microscopy (TEM), and the compositions of the films were determined by Auger electron spectroscopy (AES). The resistivity was measured by the four-probe method.

3. Results

3.1. Structure of Ni-C composite films

The color of the Ni-C films deposited at low CH_4 flow rates was the same as that of pure metal films, with the increase in CH_4 flow rate, the color of the films changed from silver to gray and dark gray but all with metallic luster. Fig. 1 shows the electron diffraction patterns and TEM bright field images of Ni-C composite films deposited at varied CH_4 flow rates, whereas the H_2 flow rate was fixed to 25 sccm. And all the

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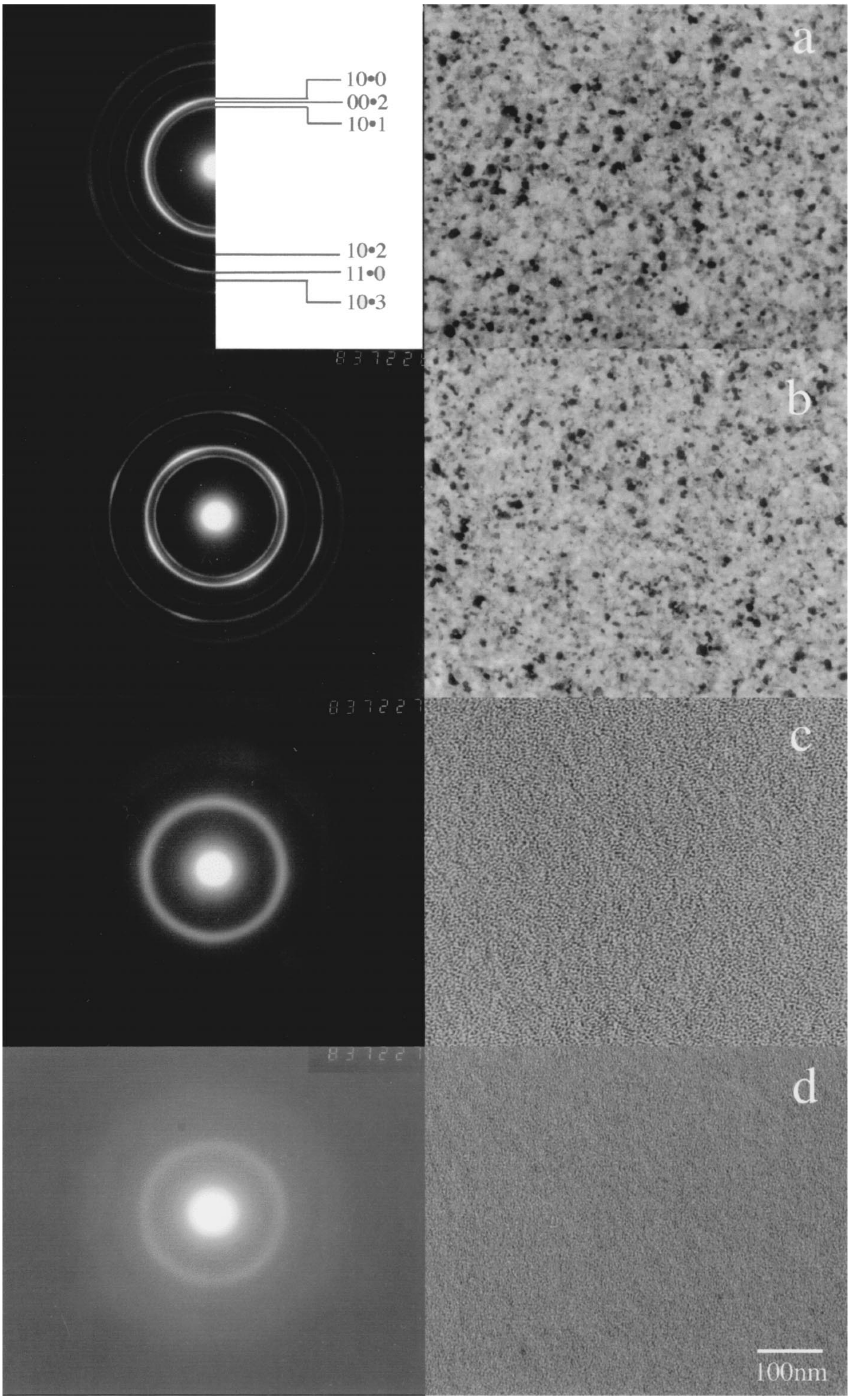

Figure 1 Electron diffraction patterns and TEM bright field images of Ni-C films deposited at ambient temperatures with CH_4 flow rate of (a) 0.1 sccm, (b) 0.2 sccm, (c) 0.35 sccm and (d) 0.5 sccm.

films were deposited at ambient temperatures which were about 50 °C, without intentionally heating the substrates. The indexing results of the diffraction pattern shown in Fig. 1a confirm the formation of Ni_3C carbide in the film, which is a phase with hexagonal close-packed (hcp) structure. No reflection from Ni can be observed in the diffraction pattern, indicating that the Ni in the film reacted with carbon completely. Increasing the CH_4 flow rate to 0.2 sccm did no change the crystal structure of the Ni-C film because the film deposited at such condition exhibits similar diffraction pattern (Fig. 1b) with that shown in Fig. 1a. When the CH_4 flow rate was increased to 0.35 sccm and above, the electron diffraction patterns do not exhibit any sharp diffraction ring due to the Ni_3C carbide, broad halos take the place of the rings. The halos appear covering the positions of 0.1 reflection of the hexagonal close-packed (hcp) Ni_3C carbide and 111 reflection of the face centered cubic (fcc) Ni phase. These results indicate that the films deposited with a CH_4 flow rate of 0.35 sccm and above are amorphous.

For films deposited with the CH_4 flow rate below 0.35 sccm, the crystallites of Ni_3C carbide of less than 10 nm in diameter can be seen clearly in the TEM bright field images (Fig. 1a and b), and the size of these crystallites decrease slightly with increasing the CH_4 flow rate. With the change of film structure from nanocrystallites to amorphous, the microstructure of the films also changed abruptly. The amorphous Ni-C film reveals much finer and uniform microstructure compared with nickel carbide nanocrystallite films, and a comparison of Fig. 1d and e shows that the microstructure became even finer with increasing the CH_4 flow rate.

All the films deposited at 200°C are composed of Ni_3C carbide as can be seen from the diffraction patterns and indexing results. The TEM images in Fig. 2 also illustrate that these films reveal granular structures with Ni_3C granules, and the size of these granules decreases with increasing the CH_4 flow rate. Compared with those deposited at ambient temperatures, these films are characterized by some thin inter-granule regions with light contrast, which are possibly composed of amorphous carbon. The enlargement of the image shown in Fig. 2a is given in Fig. 3. This further confirms the existence of such inter-granule regions as indicated by arrows in the image.

Fig. 4 shows the change of relative nickel content in the film and deposition rate with CH_4 flow rate for

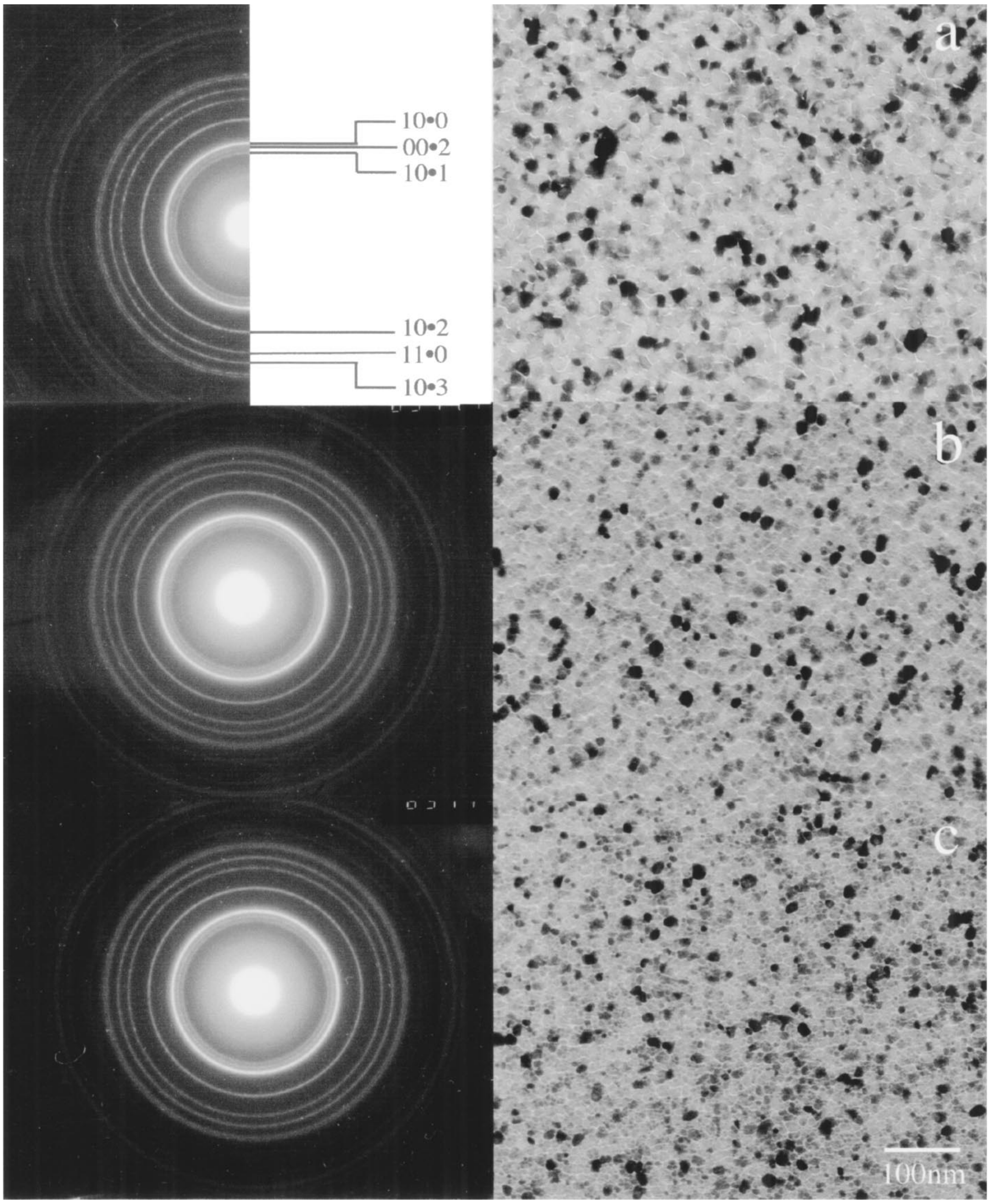

Figure 2 Electron diffraction patterns and TEM bright field images of Ni-C films deposited at ambient temperatures with CH_4 flow rate of (a) 0.02 sccm, (b) 0.2 sccm and (c) 0.35 sccm.

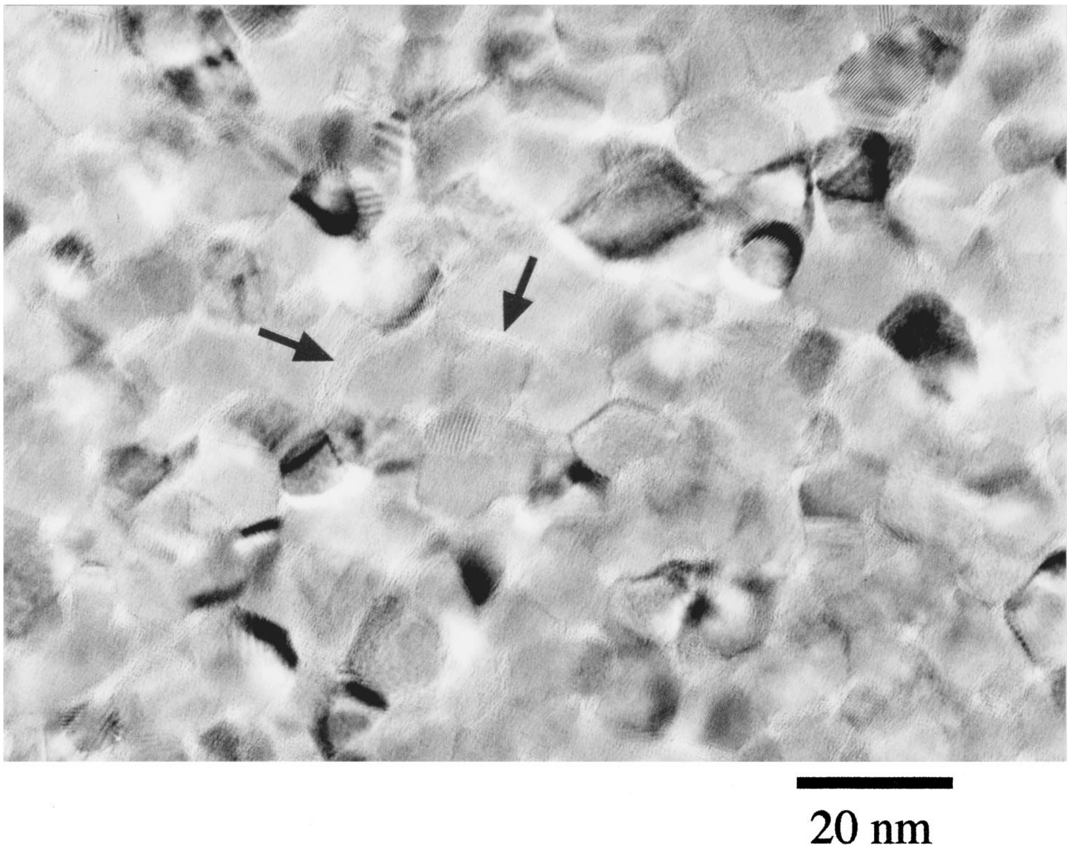

Figure 3 HRTEM image of Ni-C film deposited at 200 °C with a CH_4 flow rate of 0.02 sccm. The arrows indicate the inter-granule amorphous carbon.

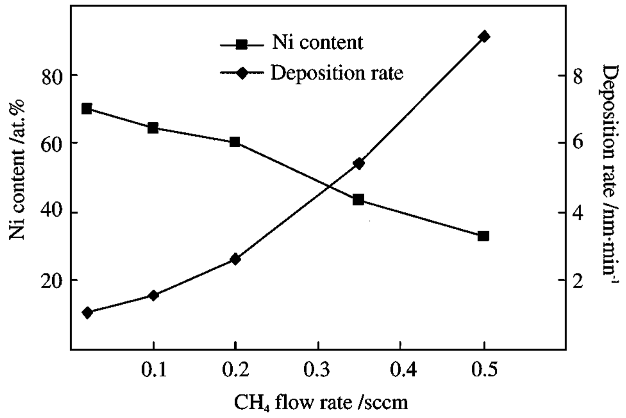

Figure 4 Dependence of Ni content, deposition rate for Ni-C films on the CH_4 flow rate.

films deposited at ambient temperatures. The relative nickel content decreases almost linearly with increasing CH_4 flow rate. It should be noted that the deposition rate and absolute load of Ni in the films were fixed for all the films, therefore this result indicates that the absolute content of carbon in the film increases with increasing CH_4 flow rate, and this leads to the increase of the deposition rate of Ni-C films. The deposition rate increases monotonically with a close to a parabolic law over the considered range of CH_4 flow rate.

3.2. Electrical properties of Ni-C composite films

Fig. 5 shows the change of resistivity of Ni-C films with CH_4 flow rate and deposition temperature. For films deposited at ambient temperatures, the resistivity increases gradually with the CH_4 flow rate below 0.2 sccm, and thereafter the resistivity goes up abruptly with increasing the CH_4 flow rate, which is the same tendency as deposition rate with CH_4 flow rate shown above. This increase of resistivity can be explained by the increase of carbon content in the films and the change of film structure from nanocrystallites of Ni_3C to amorphous. On the other hand, the granular Ni-C films deposited at 200°C reveal gradual increase in resistivity with increasing CH_4 flow rate. It should also be noted that the resistivity of Ni-C films deposited at 200°C is lower than that of films deposited at ambient temperature, because of the relatively large size of Ni_3C crystallites.

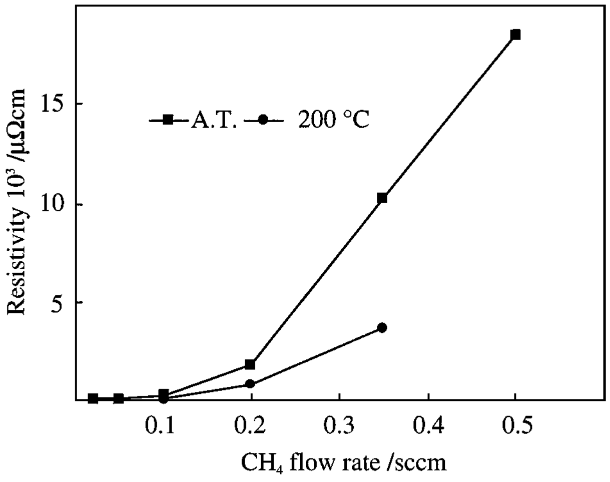

Figure 5 Dependence of resistivity of Ni-C films on the CH_4 flow rate. A.T. in the figure stands for ambient temperature.

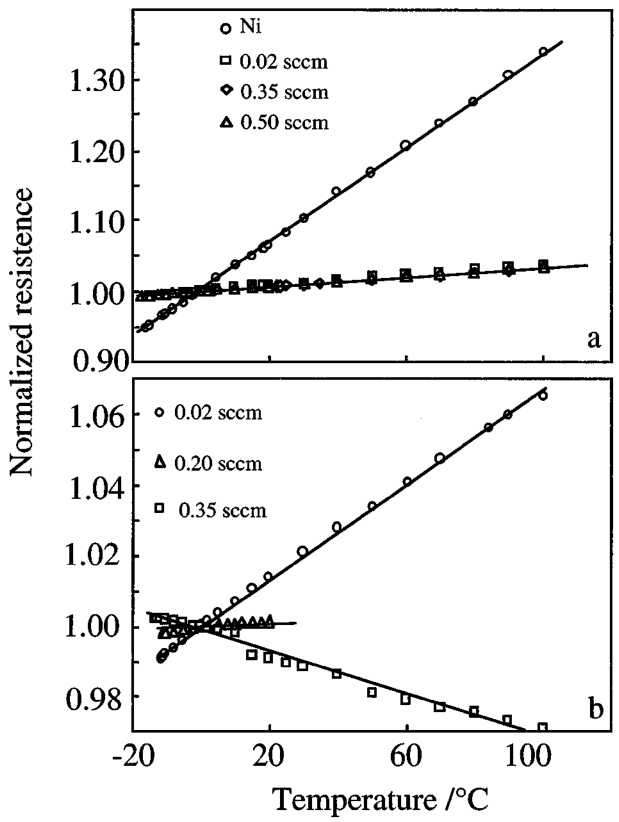

Figure 6 Temperature dependence of normalized resistence of Ni-C films deposited at (a) ambient temperature and (b) 200 °C.

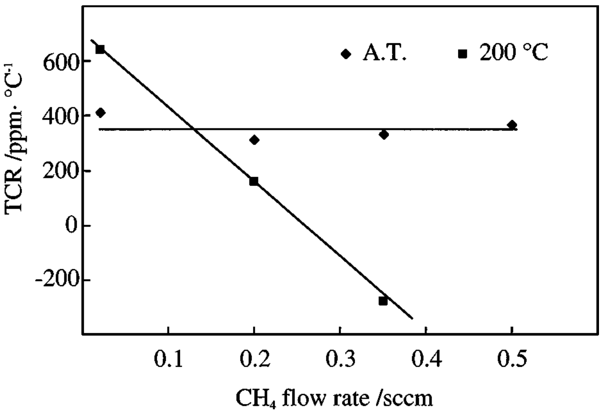

Figure 7 Relationship between TCR value and the CH_4 flow rate. A.T. in the figure stands for ambient temperature.

Fig. 6 shows the temperature dependence of normalized resistance of Ni-C films deposited at ambient temperatures and 200 °C. In Fig. 6a, the result for pure Ni film is also shown for reference. Values of temperature coefficients of resistance (TCR) for Ni-C films are shown in Fig. 7. It can be seen from Fig. 6a, Ni-C films deposited at ambient temperature show very low TCR values compared with that of metallic nickel film, nevertheless, all the films show ohmic characterization even for those in the amorphous state with very high resistivity. Besides, the TCR value does not change with increasing the CH_4 flow rate. While for films deposited at 200 °C, the TCR value decreases with increasing the CH_4 flow rate, especially, it changes the sign from positive to negative at a CH_4 flow rate of 0.35 sccm. This suggests that different processes are involved concerning the conduction mechanism.

3.3. Crystallization of amorphous Ni-C films

The crystallization behavior of amorphous Ni-C film was studied by annealing the films in a vacuum furnace ($<3 \times 10^{-4}$ Pa). Fig. 8 shows the electron diffraction patterns and TEM bright field images of the films annealed at various temperatures for 3 hours. For the films annealed below 300 °C, no perceivable change was observed either in the diffraction pattern or in the microstructure. When the film was annealed at 300 °C, the diffraction pattern shows several weak, broad, but recognizable diffraction rings, which can be identified to be the diffraction rings from the Ni_3C carbide and Ni (Fig. 8a). At this stage, the crystal sizes of Ni_3C and Ni are still not large enough to be visible in the bright field image. However, the film surface lost its original flatness because of the volume change caused by the transformation from amorphous to crystalline phases. For the film annealed at 400 °C, the diffraction rings from the Ni_3C carbide phase disappeared, and the diffraction rings from the fcc Ni phase became stronger, but still relative broad, indicating that the crystal size is still very small. In addition, the weak reflection from graphite begins to appear in the diffraction pattern, as a result of the decomposition of Ni_3C. Further increase in annealing temperature causes the increase of the Ni crystallites both in size and number. When the film was annealed at 600°C, a structure of Ni crystallites, several tens nanometers of size, uniformly dispersed in a amorphous carbon matrix, is seen from the bright field image.

According to these results, the crystallization process took place in the following sequence: in the temperature range from 300 to 400°C, very fine particles of Ni and Ni_3C precipitate from the amorphous phase and then at around 400°C, the Ni_3C carbide decomposes into Ni and graphite; thereafter, nickel precipitates gradually from the amorphous phase and the Ni particles keep growing, this can be seen from the light contrast around Ni particles. Therefore, from these results we conclude that the amorphous Ni-C phase is rather stable and does not show distinct crystallization temperature.

4. Discussion

According to the experimental results, we can see that deposition at lower CH_4 flow rate and higher temperature favors the formation of Ni_3C, which is a nonequilibium carbide phase [13–15]. While deposition at higher CH_4 flow rate and lower temperature favors the formation of Ni-C amorphous phase. Generally, it is extremely difficult to synthesize metal-carbon amorphous alloys by conventional methods such as splash-cooling, because of the high melting temperature of carbon. For example, a study has shown that even with the addition of another metalloid (eg. silicon), there was no amorphous phase formed in the Ni-C-Si system by conventional method [16]. The mechanism for the formation of Ni-C amorphous phase in the present work is considered to be associated with the high deposition rate of carbon when deposited at higher CH_4 flow rates. As stated above, the carbon content and deposition rate increases with increasing the CH_4 flow rate. Therefore

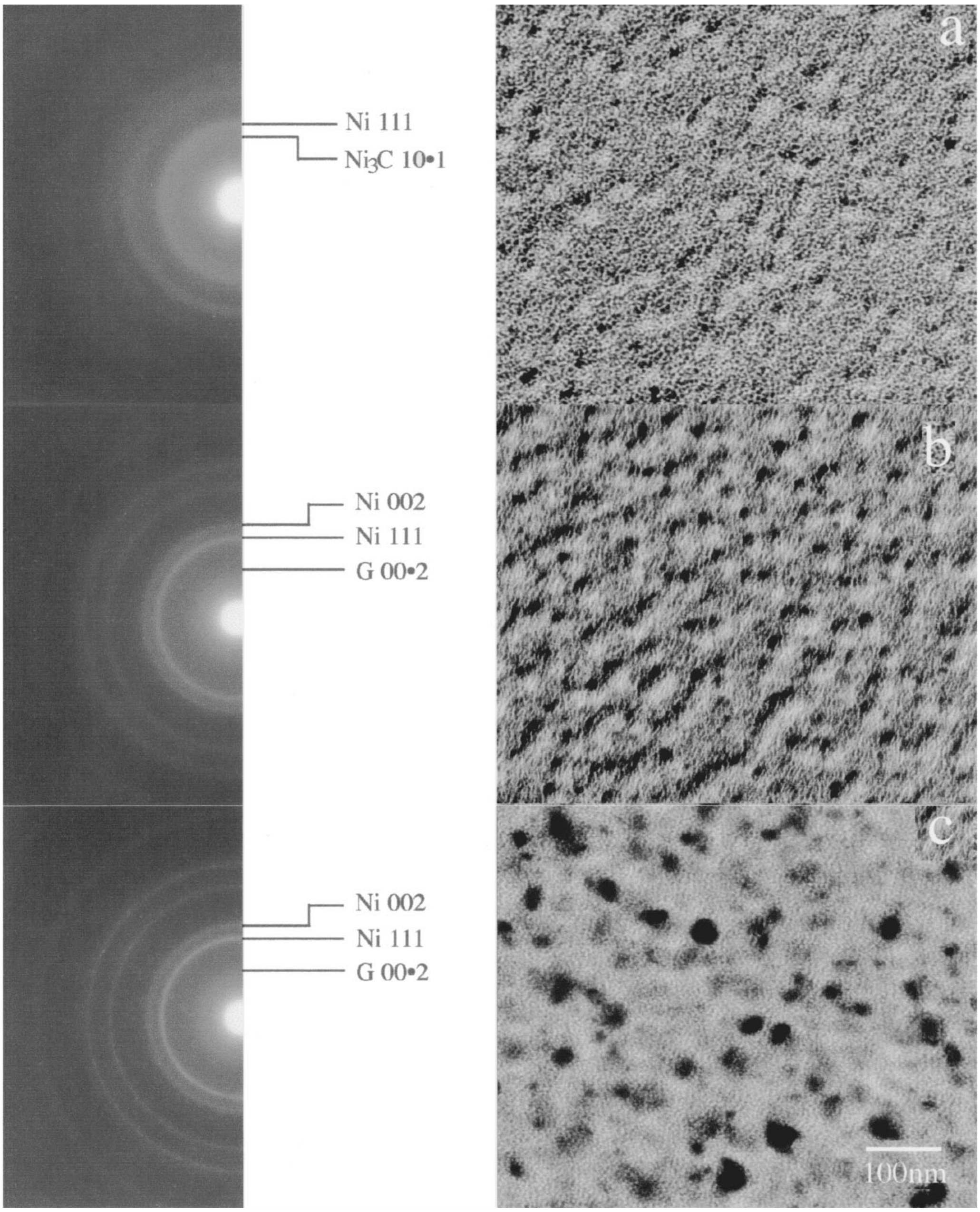

Figure 8 Electron diffraction patterns and TEM bright field images of amorphous Ni-C film after annealing at (a) 300 °C, (b) 400 °C and (c) 600 °C. The original film is shown in Fig. 1c.

we consider that the reaction between Ni and C is suppressed by the fast growth of carbon. Although short range arrangement may be formed in the film in the form of Ni and/or Ni_3C clusters during deposition process, the fast growth of carbon will prevent them from further growing, and thus the formation of amorphous Ni-C phase is promoted.

As shown in Figs 5 and 7, the Ni-C films deposited at ambient temperatures show high resistivity and low TCR values, especially for the amorphous Ni-C films. Both the high resistivity and the low TCR value can be explained by the small electron mean free path (MFP) within the film [17]. The strong scattering of conduction electrons in the present Ni-C films is considered to be caused by the large amount of disorder, very fine grain size, inclusion of amorphous carbon for the Ni-C films with Ni_3C crystallites and structural disorder for the amorphous Ni-C films. According to [18], the behavior of electrical conduction in a material with low TCR can be understood to a great deal if it is assumed that in these materials a lower limit of electron mean free path is reached. Such limit must exist because the MFP can not be smaller than the interatomic distance. If this limit is reached, further decrease in MFP due to phonon scattering is impossible. This may explain the low and almost constant TCR value for the films deposited at ambient temperatures.

On the other hand, Ni-C films deposited at 200 °C have relative low resistivity . However the TCR value of such films drops abruptly to a negative value with increasing CH_4 flow rate (Fig. 7), indicating the conduction behaviour changes to non-ohmic for the film deposited at high CH_4 flow rate. This can be explained in view of the change of films structure. As stated above, when deposited at 200 °C, the amorphus carbon are distribute at inter-granule region (Fig. 3). Therefore, with increasing the CH_4 flow rate, more amorphous carbon will be incorporated into the film, and thus leading to the encapsulation of all the Ni_3C granules by amorphous carbon at certain CH_4 flow rate. The amorphous carbon incorporated into such films are found to be glassy carbon composed mainly of sp^2 hybridization in the form of disordered graphite [4]. Therefore in Ni-C films, when all the metallic granules are encapsulated by such amorphous carbon, the films show semiconductive characteristics.

5. Conclusions

Ni-C composite films have been prepared by a codepositiion method using ion beam sputtering and microwave plasma chemical vapor deposition. It has been found that the structure and electrical properties depend strongly on the flow rate of reaction gas (CH_4) for the deposition of carbon, and the substrate temperature. The structure of Ni-C film deposited at ambient temperatures changes from nanocrystallites of Ni_3C to amorphous Ni-C alloy with increasing the CH_4 flow rate. The resistivity of the Ni-C film also increases abruptly, but all the films show ohmic conduction behaviour with very low temperature coefficient of resistance.

The Ni-C amorphous phase remains stable below 300 °C. Annealing at 300 °C and above causes the crystallization of Ni, and a structure of nanocrystallites of Ni distributed in amorphous carbon matrix is formed finally.

Granular films with Ni_3C granules and inter-granule amorphous carbon are formed for Ni-C films deposited at 200 °C. The conduction behaviour of such films changes from ohmic for the films deposited with low CH_4 flow rate to semiconductive for the films deposited with high CH_4 flow rate, due to the encapsulation of metallic Ni_3C granules by amorphous carbon.

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