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Characteristics of nickel-containing carbon films deposited using electron cyclotron resonance CVD

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Abstract

Two sets of nickel-containing carbon (Ni-C/H) films were deposited using an electron–cyclotron resonance chemical vapor deposition system in conjunction with two biased screen grids. The films were characterized using Raman scattering. Their resistivity and hardness were evaluated as a function of the gas flow ratio (CH_4/Ar). Rutherford back scattering analysis showed that the atomic fraction of Ni incorporated in the films decreases drastically from 35 to 1.4%, following increase in the CH_4/Ar ratio. Correspondingly, the film resistivity increases by 11 orders of magnitude. In contrast, the hardness decreases and the film with a Ni atomic fraction of 12% has a hardness of approximately 16 GPa. Vacuum annealing at 200 °C for 1 h immediately after the film deposition resulted in an increase in resistivity. The threshold field for field emission decreases with decreasing Ni incorporation in the film and a value of approximately 4 V/μm can be obtained for the film with the lowest Ni atomic fraction of 1.4%.

Keywords: Carbon; CVD; Nickel; Field emission

1. Introduction

Metal-containing carbon (Me-C/H) films are being widely studied and have been shown to exhibit small friction values, good conductivity, low abrasive wear rates and enhanced adhesion to metal substrates compared to pure DLC films [1,2]. The metal in these films can be introduced by many techniques [3–7]. The technique used in our study is based on an electron cyclotron resonance chemical vapor deposition (ECR-CVD) system in conjunction with two metal grids situated within the deposition chamber [8]. Compared to other techniques [1,2], our deposition technique is flexible since the grids, instead of one of the electrodes, are used as the source of the metal. This implies that it can be easily extended for the deposition of other Me-C/H films. In addition, such a system allows an independent control of the plasma ionization and the metal sputtering rates, through the microwave power and the grid bias, respectively. This is in contrast to the commonly used glow discharge sputtering technique where the two important growth parameters are correlated through the rf power [1,2].

In our previous paper [8,9], we have studied in detail W- and Mo-C/H films deposited using the above technique. In this article, results from two sets of Ni-C/H films deposited at different CH_4/Ar ratios are presented. The two sets of Ni-C/H films were deposited under identical conditions, with one subjected to thermal annealing in vacuum to investigate their thermal stability and field emission behavior.

2. Experiment

The details of the setup used in this study can be found elsewhere [8]. When a gas mixture of Ar and CH_4 is introduced into the excitation chamber through the gas inlet, a plasma is formed due to the excitation by the microwave power and the divergent magnetic field. An electric field created by the DC bias applied at the screen grids helps to direct the plasma into the deposition chamber through the Ni screen grids. In the process of passing through the screen grids, sputtering

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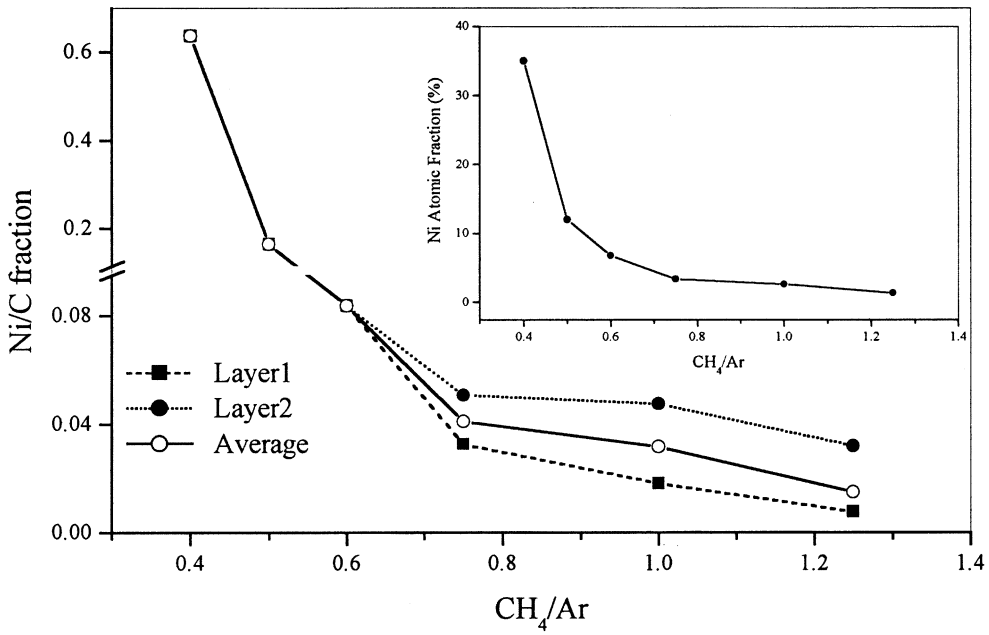

Fig. 1. The Ni/C fractions of the samples deduced from RBS as a function of the CH_4/Ar ratio. Two layers fitting with different fractions are required for samples deposited with $CH_4/Ar = 0.75$, 1.00 and 1.25. The average Ni, shown in the inset, and Ni/C fractions for these samples were computed, taking into account the thickness of the individual layers.

of Ni from the grids by Ar^+ takes place. The sputtered Ni is then incorporated into the growing films, which are deposited on substrates of (100)-oriented single crystal silicon and corning glass. For all the depositions in this study, the total chamber pressure was maintained at 8 mtorr, and a microwave power of 400 W was applied. The two screen grids were shorted to a DC voltage of −330 V, and the rf power applied to the sample was maintained at 60 W, resulting in increasing rf-induced DC bias ranging from −100 to −135 V over the CH_4/Ar ratio of 0.4–1.25. Prior to deposition, the chamber was evacuated to below 5×10^{-6} torr using a turbomolecular pump. No deliberate heating was applied to the samples during the deposition process, and the sample temperature was estimated to be 50–60 °C during growth. For samples that underwent annealing, they were heated to 200 °C for 1 h in a vacuum environment of 5×10^{-6} torr immediately after deposition without exposure to air.

3. Results and discussions

Fig. 1 shows the Ni/C fraction deduced from RBS for the Ni-C/H films at different CH_4/Ar ratios. It is found that the Ni/C fraction decreases with increasing CH_4/Ar ratio, attributed to a decrease in the sputtering rate of the Ni grids at lower Ar partial pressures. The samples at $CH_4/Ar = 0.75$, 1 and 1.25 reveal a two-layer structure with different fractions of Ni incorporated in each layer. For the two-layer structure samples, layer 1 refers to the top layer whereas layer 2 refers to the layer next to the substrate. The average Ni fraction, shown in the inset, and the average Ni/C fraction for these samples were computed, taking into account the thickness of the individual layers. At high CH_4/Ar ratio, the sputtering rate at the grids will be lower, and consequently the grids are increasingly coated by carbon. This in turn will further reduce the sputtering rate, leading to the formation of the layered structure observed, with the top layers (layer 1) having a smaller fraction of Ni incorporated.

Fig. 2 shows the Raman spectra of the Ni-C/H films at different CH_4/Ar ratios, measured using a SPEX1400 Raman system with the 514.5-nm line of an Ar^+ laser as the excitation source. Two characteristic peaks of a-C/H, the G and D peaks, can be clearly seen in the Raman spectra. The intensity of the two peaks increases with the CH_4/Ar ratio, revealing the characteristics of glassy carbon [10]. The D peak at approximately 1350 cm^{-1} is much more pronounced compared with that of Mo-C/H films [11]. This can be attributed to the difference in the impinging ion energy during film growth, which ranges from −100 to −135 V for the Ni-C/H films, compared to the lower bias of −90 V for the Mo-C/H films. A higher DC bias (magnitude) at substrates will result in more energetic ions impinging onto the substrates, which amorphizes the films and promotes the growth of sp^2 bonded carbon. Indeed, Mo-C/H films deposited at higher DC bias above −105 V also exhibited pronounced D peaks [12].

Hardness measurement, by nanoindentation technique using the Nanoindenter II from Nano Instruments, Inc.,

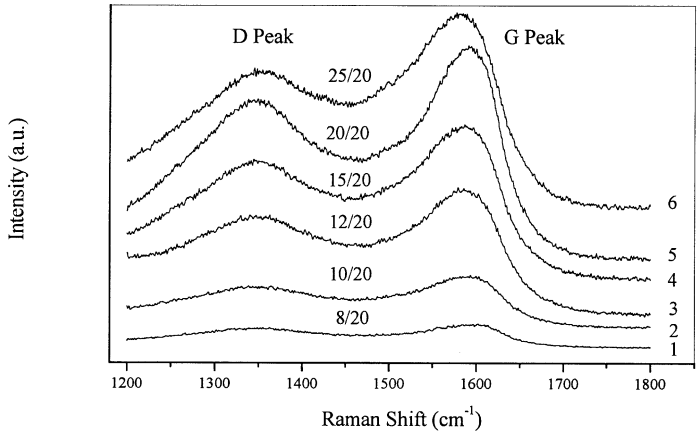

Fig. 2. The Raman spectra of the Ni-C/H films deposited at different CH_4/Ar ratios.

was performed for the films deposited on silicon substrates. The results shown in Fig. 3 are the average values measured at six different locations. It is found that the film hardness decreases from ~16 to ~8 GPa following an increase in the CH_4/Ar ratio. Compared to metal-free a-C/H films grown under the same process conditions with hardness of approximately 10 GPa, the results clearly suggest that Ni incorporation increases the film hardness. Similar results were also observed in our Mo-C/H films [8].

Fig. 4 plots the resistivity against the CH_4/Ar ratio for both the as-deposited and annealed Ni-C/H films on glass substrates. It is found that the resistivity for both sets of films increases sharply by 11 orders of magnitude with increasing CH_4/Ar ratio from 0.4 to 0.75, beyond which saturations occur. The sharp increase in resistivity with the CH_4/Ar ratio was also observed in our W- and Mo-C/H films [8,9], and was similarly reported for Ru-, Ta-, Co- and Au-C/H films at low metal fractions [1,2,13]. This indicates that the incorporated metal, even at low atomic fractions, plays a very important role in determining the film resistivity. At lower CH_4/Ar ratio, there will be more Ni atoms being incorporated in the films, leading to the lower resistivity observed. It is noted that the film at $CH_4/Ar = 0.4$ has a resistivity as low as approximately 10^{-4} Ωcm, comparable to that of metals, whereas the film at 0.75 exhibits insulating behavior with a resistivity of nearly 10^8 Ωcm. After annealing, a slight increase in the film resistivity was observed, which can be probably attributed to a denser structure in the annealed films.

The field emission measurements were carried out in other universities, therefore, only annealed Ni-C/H films were selected for such measurements, in a parallel plate configuration with an indium tin oxide (ITO) anode and an anode–cathode spacing of 100 μm in a test chamber maintained at 10^{-7} torr by an oil-free turbo-molecular pump. A conditioning process was carried out to initiate stable emission from the Me-C/H films under test. Fig. 5a plots the emission current (I) vs. electric field (E) for the Ni-C/H films with different Ni contents. It is clearly seen that the emission current increases rapidly with the field when a minimum field is reached, and

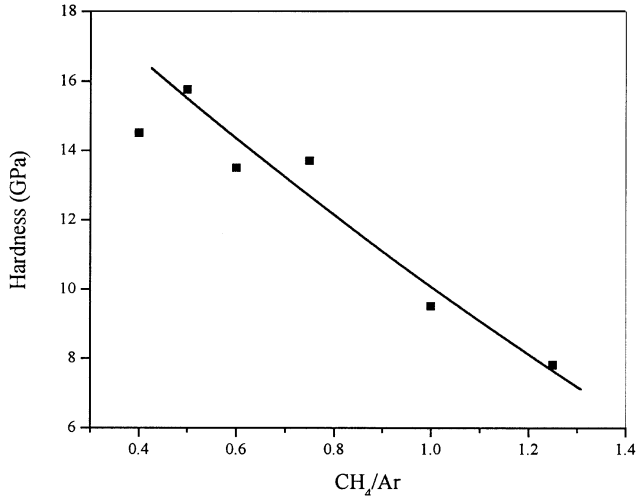

Fig. 3. The film hardness as a function of the CH_4/Ar ratio.

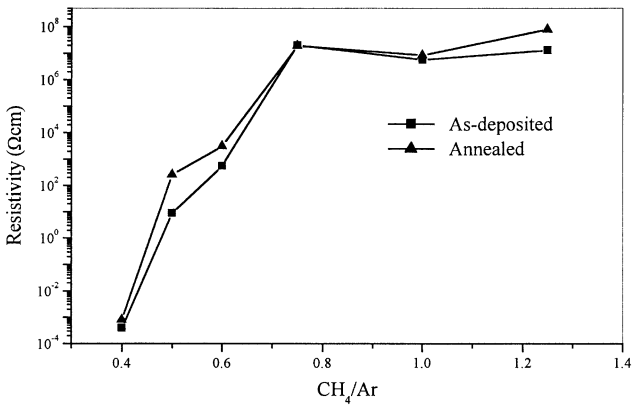

Fig. 4. The film resistivity as a function of the CH_4/Ar ratio.

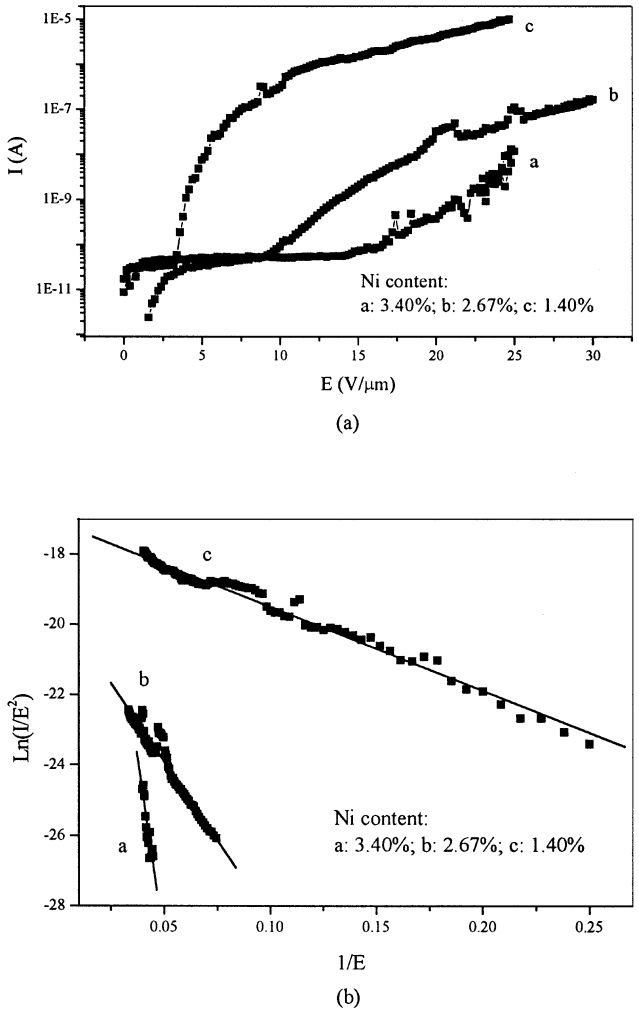

Fig. 5. Emission current vs. electric field characteristics (a) and Fowler–Nordheim plots (b) of Ni-C/H films with Ni atomic fraction of: (a) 3.40%; (b) 2.67%; and (c): 1.40%.

that the emission current from the films with low Ni content is higher. The threshold field (E_{th}), a macroscopic electric field, which gives an emission current of 1 nA for a conditioned film, is found to decrease following the decrease in the Ni content. The E_{th} is 3.95, 13.42 and 21.5 V/μm, corresponding to the Ni atomic fraction of 1.4, 2.67 and 3.4%. These results are interesting and rather different from what we have originally expected in which the emission current should be higher, while the E_{th} should be lower if the Ni incorporation is increased. It is thought that in our Me-C/H films with an ohmic back contact, the field emission is determined by both the bulk and surface of the Me-C/H films. The electrical conductivity of the three Ni-C/H films, deposited at $CH_4/Ar = 1.25$, 1.0 and 0.75, respectively, exhibits insulating characteristics, as shown in Fig. 4. In this case, the sp^2 and Ni clusters are two critical factors that determine the conductivity of the Ni-C/H films. The effective field in the Ni-C/H films will be much higher than the applied field in Fig. 5a due to the presence of these conductive clusters. Indeed, Amaratunga et al. [14] attributed the enhancement in emission from nitrogen-containing hydrogenated amorphous carbon (N-C/H) films as the N content increases, to an increase in the concentration of ionized donor (N in this case) centers which led to a higher field across the films at a given applied voltage between the n^{++}-Si and metal anode. If such a similar mechanism were present in our samples, then the higher Ni content would result in a higher field across the film. Consequently, a lower threshold and higher emission current at a same applied field will be expected. However, such a behavior was not observed in our Ni-C/H films. This suggests that the enhanced field due to the presence of sp^2 and Ni clusters does not predominantly control the field emission in the Ni-C/H films, and that there must exist other mechanisms regulating their field emission behavior. The surface roughness can also greatly influence the field emission in the Ni-C/H films. However, atomic force microscopy (AFM) image reveals a smoother surface for the present three Ni-C/H films, suggesting that the big difference in E_{th} is unlikely due to the surface roughness. The Ni-C/H films were annealed immediately after deposition without exposure to air. The residue of the reactant gases (Ar and CH_4) and the hydrogen that was used as pretreatment gas before deposition will affect the surface features such as surface barrier and passivation of molecules on the surface during film annealing. It is speculated that the surface of the film with low Ni content contains much higher hydrogen termination, which is favorable for field emission [15–17].

The linear dependence between $\ln(I/E^2)$ and $1/E$, as shown in Fig. 5b, suggests that the field emission in our Ni-C/H films follows the Fowler–Nordheim (FN) relationship [18]:

$$I = A_0 E^2 \exp[-B\Phi^{3/2}/(\beta E)] \quad (1)$$

where I is the emission current in A; E is the electric field in V/m; A_0 and B are constants; β is the dimensionless field enhancement factor; and Φ is the effective barrier height in eV. It is thought [17,19,20] that the local field enhancement, caused by various factors such as local chemical non-homogeneity, sp^2 clusters and charge localization induced by disorder, leads to electron emission. Thus, the higher the β is, the easier the emission will happen. Since the Φ in amorphous carbon films is almost constant (~5 eV [17]), the smaller slope in Fig. 5b for the film with Ni content of 1.4% means a higher β, which results in a lower threshold and higher emission current.

4. Conclusions

Two sets of Ni-C/H films were deposited using a technique based on an ECR-CVD system in conjunction

with two metal grids situated within the deposition chamber. The films deposited at higher CH_4/Ar ratios show a two-layer structure, and the average Ni atomic fractions in the films decrease drastically from 35 to 1.4% following an increase in CH_4/Ar flow ratio. The hardness also decreases with increasing CH_4/Ar flow ratio, and the film with a Ni atomic fraction of 12% has a hardness of approximately 16 GPa. The resistivity increases by 11 orders of magnitude following the decrease in Ni atomic fraction. The films annealed at 200 °C exhibit a slight increase in their resistivity. The local field enhancement is responsible for the electron emission of our Ni-C/H films. The higher β for the film with the lowest Ni atomic fraction of 1.4% leads to a threshold field of approximately 4 $V/\mu m$.

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