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Investigation of tungsten incorporated amorphous carbon film

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Abstract

Metal incorporated carbon films (Me-C:H) were deposited using a new technique with two W screen grids incorporated inside an electron cyclotron resonance chemical vapour deposition (ECR-CVD) chamber. This technique is versatile when applied to the deposition of Me-C:H films as the degree of plasma ionisation, the sputtering rate of the metal grids and the energy of the impinging ions can be independently controlled. In this work, the proposed technique is demonstrated through W-C:H deposition at different flow ratios of CH_4 to Ar. A DC bias of − 330V was applied to the upper and lower grids with either the substrate floating or under direct DC bias. The films were characterised in terms of their conductivity, atomic concentration (RBS), atomic configuration(XPS and XRD), hardness and optical absorption. The resistivities and the optical gaps of the films were noted to decrease drastically upon incorporation of several atomic percentage of W. WC formation is only observed for films deposited with the substrate under direct DC bias.

Keywords: Tungsten; Amorphous Carbon film; electron cyclotron resonance chemical vapour deposition

1. Introduction

Diamond-like carbon (DLC) films have generated scientific interest due to their unique properties such as chemical inertness, mechanical hardness, excellent wear properties and low friction coefficient [1]. A main disadvantage of DLC films is their high stress values that lead to peel off and poor adhesion especially on metal substrates. It has been shown that the range of technical applications of these films can be greatly enhanced by doping them with metals [1]. These metal incorporated DLC films with properties intermediate between diamond-like carbon (DLC) and metal carbides have been shown to have small friction values, an extremely low abrasive wear rates and good adhesion to metal substrates that could be better than DLC [2,3]. These films were also found to exhibit interesting electrical properties, with their conductivities varied over many orders of magnitude upon incorporation with a small fraction of metal.

In this paper, we present a new technique for depositing Me-C:H films base on an electron cyclotron resonance chemical vapour deposition (ECR-CVD) system. The source of metal is derived from two biased metal screen grids situated within the deposition chamber and supported above the substrate holder. Using a gas mixture of Ar and CH_4, metal can be sputtered from the biased grids by the Ar^+ ions and incorporated into the growing a-C:H films. By varying the applied bias at the grid, adjusting the heights of the grids from the substrate holder, changing the flow ratio of CH_4/Ar or using grids with different wire spacing, the amount of metal incorporated can be controlled. This metal screen grid fixture concept was originally developed for growing DLC films under direct DC bias in an ECR-CVD system[4,5], to achieve an independent control of the ionisation of the gases by the microwave power and the energy of the ions arriving at the substrates. In applying it to the deposition of Me-C:H films, the grid set up would similarly allow the flexibility of an independent control of the plasma ionisation, the sputtering rate of the metal and also the energy of the impinging ions. W-C:H films were deposited with the proposed technique in a gas mixture of CH_4 and Ar at different gas flow ratios. These films were characterised in terms of their conductivity, atomic concentration by Rutherfold backscattering (RBS) technique, bonding configuration by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), hardness and optical absorption.

2. Experiment

The details of the ECR-CVD system with the screen grid

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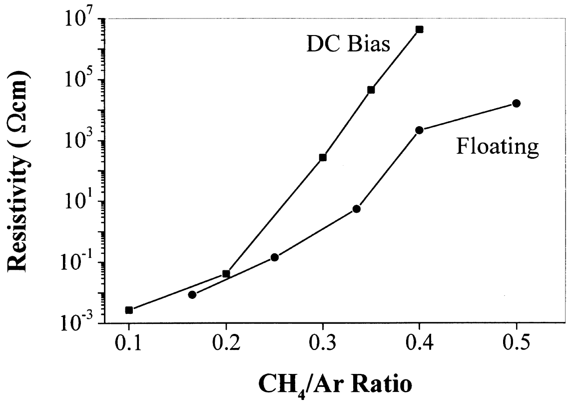

Fig. 1. The resistivity of the films measured using the four-point probe technique at different CH_4/Ar ratios for the biased and floating samples.

set up incorporated can be found elsewhere [4]. The grid fixture consisting of two pure W wire meshes is supported by four poles made of insulating Vespal. Two grids are used in this system because in the previous study on the deposition of DLC films, it was found that using only a single grid (the upper grid) without the lower grid was not effective in accelerating the ions compared to the case when both grids were present [4]. The results have been attributed to the more effective acceleration of the ions in the presence of the lower grid which maintains its surrounding plasma at a negative potential, and hence reduces the shielding effect of the positive charge build up at the substrate surface. It is possible that this undesirable effect could be less severe in this case since Me-C:H films generally have higher conductivity than DLC films. The square pure W meshes used have spacing between the W wires of about 10 mm. The distance between the lower and upper grids was fixed at 5 cm, and that between the lower grid and the sample holder was fixed at 1.5 cm in the present experiment. The lower and upper grids are shorted together to a negative DC voltage of −330 V, and the substrate holder was either floating with no DC biasing or with a DC bias of −50 V applied. In this experiment, CH_4 to Ar flow ratio was varied from 0.15 to 0.5 with the pressure maintained constant at 6 mTorr. The microwave power used was fixed at 400 W and the depositions were carried out at room temperature. The substrates used consist of glass and (100)-oriented single crystal silicon.

3. Results

Fig. 1 shows the resistivity of the films measured using the four point probe technique at different CH_4/Ar flow ratios for both cases of floating and biased substrates. It can be seen that at decreasing CH_4/Ar ratio, there is a very rapid decrease in the resistivity of the samples, attributed to the incorporation of W in the films. It is noted that in the case of biased substrates, the change in resistivity spans almost 9 orders of magnitude. In the regime of higher CH_4/Ar ratio (lower W content), the biased samples have resistivities in the range of 10^7 Ω cm, typical of pure a-C:H films. Except at lower CH_4/Ar ratio, where the resistivities of the two sets of films approached each other, the biased samples consistently have larger resistivity compared to the floating samples. Similar drastic changes in the resistivity have also been reported for Ru-C:H, Ta-C:H, Co-C:H and Au-C:H films at low metal fraction [2,3,6,7], and this has been attributed to not only the incorporation of metal in such films, but also the modification of the a-C:H matrix in terms of the different fraction of sp^2 to sp^3 bonds in the presence of metal.

RBS and XPS measurements were performed on the floating samples. Fig. 2 shows the atomic fraction of W in the films obtained using RBS at different flow ratios of CH_4/Ar. The maximum atomic fraction of W was found to about 8%, therefore these films are expected to be more semiconducting-like than metal-like in terms of their variation in electrical conductivity with temperature [6]. Fig. 3 shows the W 4f core level spectra of the floating W-C:H films with W atomic fraction of (a) 0.022 and (b) 0.085. These measurements were performed in a VG ESCALAB MkII spectrometer equipped with a Mg K_α X-ray source (1253.6 eV) and a hemispherical electron energy analyser. The take-off angle was maintained at 75° and the constant pass energy was set at 10 eV during the spectral measurement. The binding energy was referenced to the Au $4f_{7/2}$ line at 84.00 eV. The curve fitting of the XPS peaks was performed with combined Gaussian and Lorentzian curves and Shirley background subtraction. From Fig. 3, the two components of W 4f doublet appear at $BE = 35.5 \pm 0.02$ eV (W $4f_{7/2}$) and 37.6 ± 0.02 eV (W $4f_{5/2}$), indicating the incorporation of W into the a-C:H network. The bonding of W is found to be in form of WO_3 [8,9]. For the case of higher fraction of W in the films (Fig.3 (b)), the XPS spectrum shows a new component with W $4f_{7/2}$ at 33.2 ± 0.2 eV which was assigned to WO_2 [10]. The component attributed to WO_2 bonds has a weaker intensity than that from WO_3. The very small amount of W in the film and broadening of

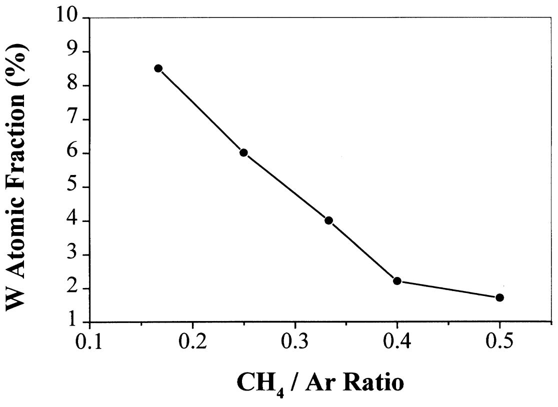

Fig. 2. The W atomic fraction of the films at different CH_4/Ar ratios for the floating samples.

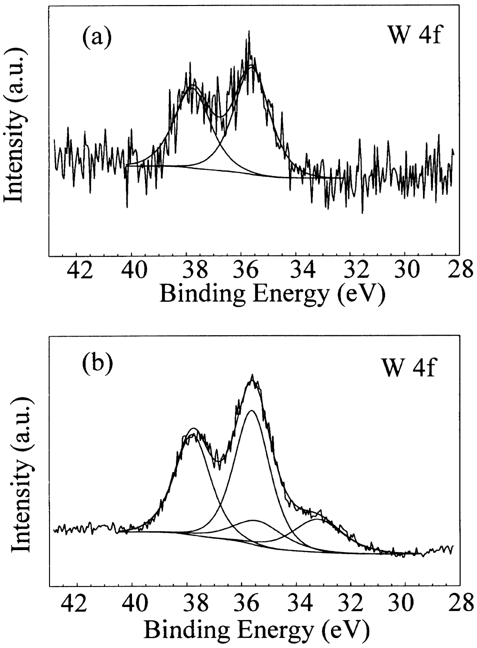

Fig. 3. XPS W 4f core level spectra of the floating W-C:H samples with W atomic fractions of (a) 0.022 and (b) 0.085.

W $4f_{7/2}$ peak at 33.2 ± 0.2 eV might limit the detection of WO_2 component (see Fig. 3a). The formation of tungsten oxides is attributed mainly to post-oxidation upon exposure in air.

No presence of WC bonds was deduced from the XPS and XRD analysis of the floating samples, which is attributed to the fact that no bias was applied to the samples during the deposition. This deduction is confirmed through XRD analysis of the biased samples which clearly reveals the presence of WC signals, as can be seen from Fig. 4 for the sample deposited at the two lowest CH_4/Ar ratios of 0.1 and 0.2. The results suggest that certain minimum amount of ion energy is required for the formation WC in these films. For the biased samples, no WC signal was observed for those samples deposited at larger CH_4/Ar ratio, due to the smaller amount of W incorporated.

The hardness of these films were measured using the Nanoindenter II system. The results showed that the biased samples have hardness of about 10 Gpa, as compared to the floating samples of about 5 Gpa. The hardness for both sets of films are found to be not sensitive to the CH_4/Ar flow ratios, and hence to the W contents. This is believed to be due to the low W content in these films such that their mechanical properties are still predominantly controlled by the a-C:H matrix, which in turn is determined by the impinging ion energy. Therefore, as in the case of pure a-C:H films, our results also suggest that the hardness of these W-C:H films are mainly determined by the ion energy during growth.

Fig. 5a shows the conductivity of the samples measured at different temperatures. With no detailed information on the exact mechanism of electronic transport in these films, the conductivity was modelled in the simplest form, namely $\sigma = \sigma_0 \exp(-E_a/kT)$. In our case, it was found that assuming temperature independent prefactor σ_0 and activation energy E_a gives rise to reasonable fit (solid lines in Fig. 5a) for most of the samples over the temperature range investigated. It should be noted that our modelling provides a measure of the degree of thermal activation in the conductivity, rather than implies any prevailing conduction behaviour in these films as the fittings were carried out only over a limited temperature range. Fig. 5b shows the deduced activation energy of the biased samples at different CH_4/Ar ratios. The results reveal thermally activated process for all the samples, with the activation energy decreases at increasing W content. Activation energy measurements were similarly performed for the floating samples, however, over a narrower temperature range from room temperature to 150°C due to these samples being thermally less stable. Therefore the activation energy of these samples cannot be accurately determined. Nevertheless, a much steeper increase in the conductivity with temperature was clearly observed for films with lower W fractions, similar to the case of the biased samples. The observed thermally activated conduction behaviour could be attributed to the tunnelling of electrons between the metal clusters, with the decrease in activation energy at higher W content indicating the transition of these films from semiconductor-like to metallic-like [6].

The optical absorption in these films are obtained using samples deposited on glass substrates, through their transmittance and reflectance measured by a Perkin–Elmer lambda 16 dual beam spectrophotometer. Fig. 5b shows the Tauc gaps (E_0) for both sets of films as a function of the CH_4/Ar ratio. Both the optical gaps decrease sharply by more than 1.5 eV over the range of CH_4/Ar ratio studied, which is certainly related to the increased absorption in the presence of W clusters. The floating samples also consistently exhibit higher optical gaps than the biased samples, which is related to their more polymeric structure, in consis-

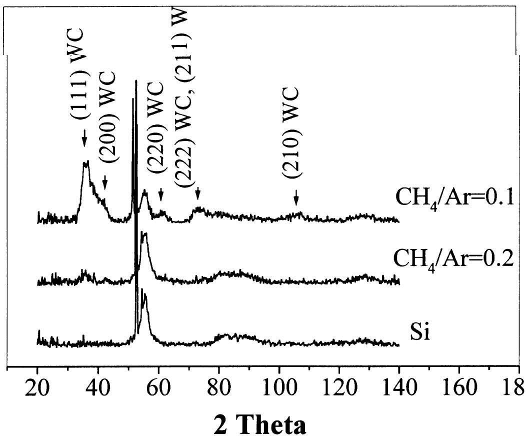

Fig. 4. XRD patterns from the biased W-C:H samples with larger W contents, at the two lowest CH_4/Ar flow ratios of 0.1 and 0.2.

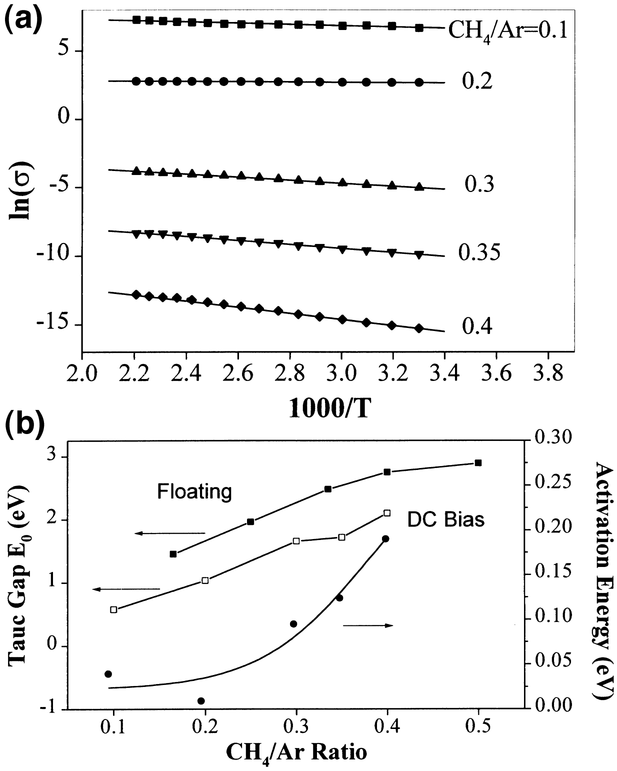

Fig. 5. (a) The conductivity of the films measured as a function of temperature. (b) Activation energy for the biased W-C:H samples and the Tauc gap (E_0) for both sets of films at different CH_4/Ar flow ratios.

tent with the hardness results. It should be noted that the large variation in the optical gap is strongly correlated to the drastic decrease observed in the resistivities of these films.

4. Discussion

The screen grid technique used in conjunction with the ECR-CVD system has been successfully demonstrated for the deposition of Me-C:H films. Utilising the highly ionised ECR plasma for the sputtering of the metal and concurrently for the film growth, the deposition process can be considered as a plasma reactive sputtering. Through varying the microwave power and the DC biased at the grids and at the substrates, the degree of the plasma ionisation, the rate of the metal sputtering and the microstructural properties of the films can be effectively and independently controlled. This, couples with the advantage of a highly ionised ECR plasma, makes the proposed technique attractive for the deposition of a wide range of Me-C:H films with very different structural properties.

Compared to other techniques [2,3], the present system 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 ionisation through the microwave power and the metal sputtering rate through the grid bias, in contrast to the commonly used glow discharge sputtering technique where the plasma ionisation and the metal sputtering rate are correlated through the RF power [2,3]. Besides through varying the applied bias at the grid and the flow ratio of CH_4/Ar, this technique also allows other ways of controlling the metal incorporation by adjusting the heights of the grids from the substrate holder and using grids with different opening size.

The main limitation of the technique comes from the coating of the grids during the deposition process, resulting in diminishing incorporation of metal in the films. It is noted that the poisoning of the target problem is also commonly encountered in other deposition techniques [11]. In our case, this could be overcome by having a very large bias at the grids to prevent the grids from being coated substantially. The fraction of the W films can then be controlled through the separation of the grids from the substrate holder or the CH_4/Ar flow ratio.

Our results on the W-C:H films deposited using the proposed system revealed the incorporation of W in these films resulting in drastic changes in their resistivities and optical bandgaps. The much larger resistivities of the biased samples at larger CH_4/Ar ratios compared to the floating samples could be related to the amount of W incorporation in the films, or to the microstructures of these films under different bias conditions. In terms of their microstructures, it is expected that the biased samples are more constrained due to their denser and more cross-linked network, as supported by the hardness results, which could discourage the incorporation of W atoms in the case of lower W fraction. However, at higher W fraction when the W clusters dominate the conduction behaviour, it was found that both the biased and floating samples exhibit similar resistivities with respect to the CH_4/Ar gas flow ratio. From the thermally activated conduction behaviour, it can be deduced that electrical conduction in these films occurs mainly through the tunnelling of electrons between the W clusters. For the range of CH_4/Ar flow ratios studied, with the largest W atomic fraction in the floating samples being 8%, it is believed that the W clusters do not yet form a continuous network. In this case, the drastic decrease in the resistivities of these films could not be totally attributed to the presence of these W clusters. Following the interpretation for Au-C:H and Ta-C:H films [6], it is proposed that the presence of W or WC modifies the structure of the a-C:H matrix and partly accounts for the sharp changes in the resistivity observed. The more reactive W in our case gives rise to the much smaller values of resistivity observed as compared to the Au-C:H films [6], even at low atomic fraction of W.

5. Conclusion

A new technique for depositing Me-C:H films based on two biased screen grids situated above the substrate holder in an ECR-CVD system has been demonstrated. This technique allows the independent control of the degree of plasma ionisation, the metal sputtering rate and the impinging ion energy, and hence can be used for the deposition of a wide range of Me-C:H films with very different microstructural properties. W-C:H films have been deposited using this technique under floating and biased substrates conditions. It was found that WC is formed only in the case of samples under DC bias. In both cases, it has been found that these films experienced drastic changes in their electrical and optical properties, with the resistivity and optical gap decreased sharply in the presence of less than 10% W atomic fraction. These films exhibit thermally activated electrical conduction behaviour, revealing a predominantly semiconducting-like characteristic.

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