

Investigation of molybdenum-carbon films (Mo-C:H) deposited using an electron cyclotron resonance chemical vapor deposition system

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(Received 18 January 2000; accepted for publication 9 June 2000)

We have recently proposed a technique for depositing metal incorporated carbon films (Me-C:H) based on an electron cyclotron resonance chemical vapor deposition (ECR) process. This technique employs an ECR plasma derived from the excitation of source gases CH₄ and Ar, together with two grids embedded within the chamber that serve as the source of the metal. It has been successfully applied for the deposition of tungsten-carbon films (W-C:H) which have been shown to exhibit a wide range of electrical, optical, and microstructural properties. These properties can be controlled through varying the deposition conditions such as the bias voltages at the grids and the substrate holder, and the flow ratio of CH₄/Ar. In this work, we report on the growth and characterization of molybdenum-carbon (Mo-C:H) films deposited using the above technique incorporating two pure Mo grids. The effect of radio-frequency induced direct-current (dc) bias at the substrates was investigated. It was found that the resistivity of the films decreased by 9 orders of magnitude, and the optical gap decreased by more than 2 eV with increasing bias voltage from -38 to -130 V. The results suggest that the substrate dc bias has a crucial effect on the incorporation of Mo into the *a*-C:H films and the resulting microstructures, with larger bias voltages leading to an increase in the Mo fractions in the films. Concurrently, the hardness of the films was found to deteriorate from 22 to 10 GPa. The structures of these Mo-C:H films were characterized using x-ray diffraction and Raman scattering. Mo was found to exist in the forms of Mo and MoC and Mo₂C. The experimental results are interpreted in terms of the effects of ion energy on the structure of the films having Mo clusters embedded within an amorphous carbon matrix. © 2000 American Institute of Physics. [S0021-8979(00)03918-9]

I. INTRODUCTION

Metal incorporated diamond-like carbon (Me-C:H) films have been actively studied due to their better adhesion and tribological properties compared to pure diamond-like carbon (DLC) films.¹ These films exhibit interesting properties intermediate between DLC and metal carbides.² Their conductivity and conduction mechanisms are very sensitive to the atomic concentration of metal incorporated.^{2,3} Recent studies of their microstructures have revealed that these films consist of nanocrystallites of metal-carbide embedded in an amorphous hydrocarbon matrix.⁴ The nanocrystalline/amorphous structures of these nanocomposite films have been shown to be responsible for the unique mechanical and tribological properties observed, such as high hardness, low friction coefficient, and high toughness.⁵

To date, several techniques have been proposed for the deposition of Me-C:H films, the most common of which include sputter deposition in a hydrocarbon and Ar gas mixture,⁶ radio-frequency (rf) magnetron sputtering,⁷ and lately by magnetron assisted pulsed laser deposition.⁵ Recently, we have demonstrated the deposition of tungsten-

carbon (W-C:H) films using a technique base on an electron cyclotron resonance chemical vapor deposition (ECR-CVD) system incorporating two W screen grids supported above the substrate holder.⁸ Sputtering of the grids by Ar⁺ ions derived from a highly excited CH₄/Ar ECR plasma provides the source of W for the deposition. As the highly ionized ECR plasma is used for the sputtering of the metal and concurrently for the film growth, we classify this deposition process as plasma reactive sputtering. This technique is versatile as it allows the flexibility of controlling many growth parameters. For example, the degree of plasma ionization can be controlled through the microwave power, the sputtering rate of the metal through the bias applied to the grids and the CH₄/Ar gas flow ratio, the energy of the impinging ions through the rf induced or direct dc bias at the substrates. Other secondary controls include varying the separation of the grid from the substrates and the grid opening size. For W-C:H films studied under the condition of no substrate bias applied, the conductivity increased by 6 orders of magnitude and the optical gap decreased by 1.5 eV with increasing atomic fraction of W in the films from 2% to 8%. W-C bonds were not detected and the W detected was mainly in the form of WO₂ and WO₃. Upon substrate biasing, a larger magnitude of conductivity change was observed and W-C

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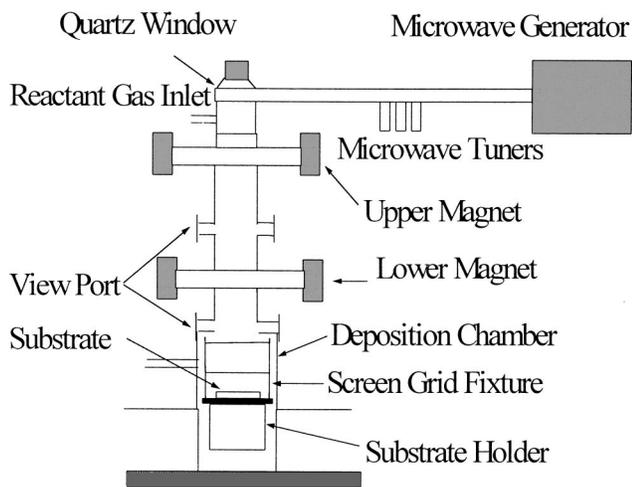


FIG. 1. Schematic diagram of the ECR-CVD system with the screen grid fixture included in the deposition chamber. The lower and upper grids were shorted to a negative dc voltage of -330 V, and the rf power applied to the substrates was varied from 0 to 125 W resulting in self-induced dc bias voltages over a range of -38 to -130 V.

nanocrystallites were also detected.⁸ The results suggest that the energy of the ions impinging onto the substrates plays a crucial role in determining the microstructure of the W-C:H films, and a certain minimum amount of ion energy might be required to promote the formation of W-C in these films.

In the present work, we report on the deposition and characterization of molybdenum-carbon (Mo-C:H) films deposited using the above technique incorporating two pure Mo grids. A detailed study of the effects of varying CH_4/Ar ratio at a constant bias voltage on the properties of Mo-C:H has been reported recently.⁹ Here we present new results on the effects of ion energy on the growth and properties of these Mo-C:H films by varying the rf-induced dc bias at the substrates. In this study, their atomic compositions, resistivity, optical absorption, hardness, Raman scattering, and x-ray diffraction are characterized. As Mo-C:H is not widely investigated to date compared to other Me-C:H films such as Ti-C:H and W-C:H,² the study will help to provide further insights into the growth and structural properties of Me-C:H films in general.

II. EXPERIMENT

The schematic diagram of the ECR-CVD system incorporating the screen grid fixture used in this work is shown in Fig. 1. The details of the ECR-CVD system can be found elsewhere.¹⁰ The grid fixture consisting of two pure Mo wire grids is supported by four poles made of insulating Vespal. The high purity Mo grids measured 100 mm by 100 mm, have wire diameter of 0.18 mm, and spacing between the wires of 0.8 mm. In the present experiment, the distance between the upper and lower grids, and that between the lower grid and the sample holder were fixed at 2.8 cm. The lower and upper grids were shorted to a negative dc voltage of -330 V, and the rf power was varied from 0 to 125 W resulting in self-induced dc bias voltages over a range of -38 to -130 V. The microwave power used was fixed at 400 W and the process pressure maintained constant at 8

TABLE I. The relative atomic fractions of Mo, O, and Ar with respect to C deduced using RBS for films deposited at different bias voltages. For samples that had two layers, layer 1 refers to the top layer whereas layer 2 refers to the layer next to the substrate. (*The data given above have ignored the content of H in the samples. The thickness given may therefore not represent the true thickness of the films.)

rf-induced dc bias (V)	Layer	Thickness (nm)*	Mo	Mo (average)	O	Ar
-130	1	84.3	0.0393	...	0.15	...
-115	1	114.0	0.0223	0.0320	0.006	0.0021
	2	39.6	0.0624		0.006	0.0022
-105	1	96.2	0.0121	0.0194	0.006	0.002
	2	54.1	0.0334		0.006	0.0021
-90	1	79.8	0.00818	0.0132	0.005	0.0066
	2	38.7	0.0239		0.005	0.0062
-65	1	68.9	0.0128	...	0.145	...
-38	1	36.2	0.0229	...	0.18	...

mTorr. The CH_4/Ar flow ratio was regulated at 15/20 sccm and the depositions were carried out at room temperature. The substrates used consist of glass and (100)-oriented single crystal silicon.

III. RESULTS

Rutherford backscattering (RBS) channeling was carried out using 2 MeV He^+ to determine the content of C, Mo, and Ar in the Mo-C:H films deposited on (100) silicon substrates. The target normal was aligned with the beam in order to achieve a channeling geometry in which the signal from the Si matrix was reduced by 1 to 2 orders of magnitude. A 50 mm² surface barrier detector mounted at 160° scattering angle was then used to collect the backscattering spectra. In this way, the sensitivity to light elements (C and O) was enhanced, because their signal overlaps with that of Si. The errors in the C and O concentrations are around 10% and that for Mo is expected to be lower. Particle induced x-ray emission (PIXE) spectra confirmed the presence of Ar, Mo, and Si (substrate) in these films. The RBS spectra of the samples deposited at -115 , -105 , and -90 V revealed a two-layer structure with different fractions of Mo incorporated in each layer. Table I shows the results obtained for Mo, O, and Ar relative to carbon for all the films. For the samples that had a two-layer structure, layer 1 refers to the top layer whereas layer 2 refers to the layer next to the substrate. The average Mo/C fractions for these samples taking into account the thickness of the individual layers are also shown. For easy reference, the Mo/C fractions are also plotted in Fig. 2. It can be seen that, except for the sample deposited at the lowest bias voltage, there is generally an increase in the average Mo fraction at increasing dc bias voltage. As the microwave power, CH_4/Ar flow ratio, and the grid bias voltage were maintained constant across all the samples, it is expected that the sputtering rate of the Mo grids remained unchanged. The results therefore suggest that larger dc bias voltages at the substrates promote an increase in the Mo fraction incorporated in the films. It is noted that Meng *et al.* have reported

Ti fractions that are relatively independent of the substrate bias for Ti-C:H films deposited using a magnetron sputter deposition system.¹¹

Figure 3 shows the x-ray diffraction (XRD) patterns measured using the Siemens D5005 x-ray diffractometer for the film deposited at the highest dc bias of -130 V. The system uses Cu K α radiation with $\lambda = 1.54 \text{ \AA}$ and the incidence angle measured with respect to the films was fixed at 4°. Besides the crystalline Si substrate peaks, other diffraction peaks corresponding to crystalline MoC(205), Mo₂C(102), and Mo(211) were noted. The spectrum is typical of those obtained for the other samples. X-ray photoelectron spectroscopy (XPS) measurement for one of the samples deposited at -90 V exhibited peaks corresponding to C 1s, O 1s, and Mo 3d. The deconvolution of the C 1s peak measured at high resolution revealed the 284.1 and 288.1 eV peaks attributed to polymeric and oxidic carbon (C-O) respectively. In addition, a component at 283.1 eV indicated the presence of Mo-C bonds. Similarly, decomposition of the Mo 3d peak gave rise to four components, two at 235.6 and 232.5 eV attributed to Mo-O bonds in different Mo oxides, and the other two at 231.5 and 228.5 eV attributed to Mo-Mo bonds of different electronic spins. The detail results of the XPS studies have been published elsewhere.¹²

Figure 4(a) shows the resistivity of the films measured using the four point probe technique for films deposited on glass at different dc bias voltages. A sharp decrease in the resistivity can be seen at increasing dc bias voltage, which is clearly related to the increase in the Mo fraction in the films. Two plateau regions in the variation of the resistivity with dc bias are observed. The one at lower bias range has resistivity in the order of 10⁸ Ω cm, which is typical of pure a-C:H films, whereas the other at larger bias voltages has very low resistivity of about 10⁻¹ Ω cm, which is about 5 orders of magnitude larger compared to that of bulk Mo. Previous study on a series of Mo-C:H films deposited at a constant substrate bias voltage and varying CH₄/Ar flow ratio revealed a change in the conductivity from about 10⁸ to 10⁻³

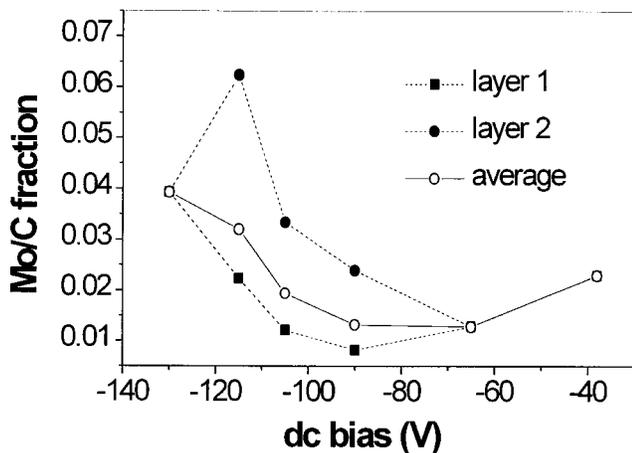


FIG. 2. The Mo/C fractions of the samples deduced using RBS as a function of the dc bias voltage. Two layers fitting are required for samples deposited at -115, -105, and -90 V (see Table I). The average Mo/C fractions for these samples taking into account the thickness of the two layers are also shown.

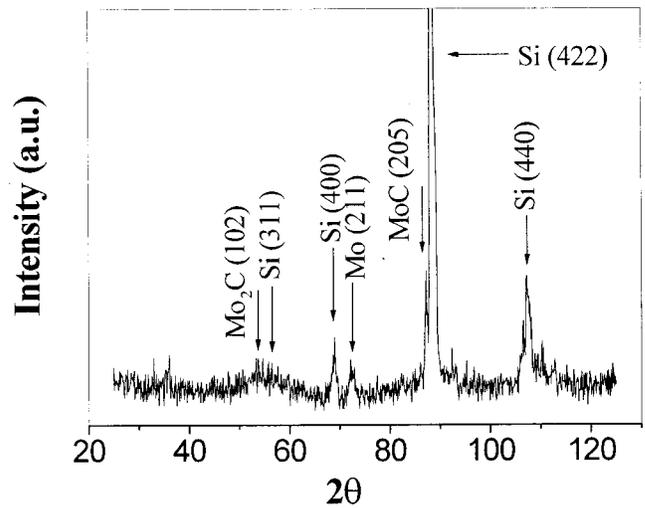


FIG. 3. XRD patterns for the film deposited at dc bias voltage of -130 V.

Ω cm when the Mo fraction, as deduced from XPS, was found to range correspondingly from about 0.3% to 15%. Consider that comparable resistivity changes have been observed in this study, however, over a smaller range of Mo fraction (see Table I), it is deduced that the resistivity of the Mo-C:H films depends not only on the fraction of Mo incorporated, but also on the microstructures of the films which are critically dependent on the applied substrate bias.

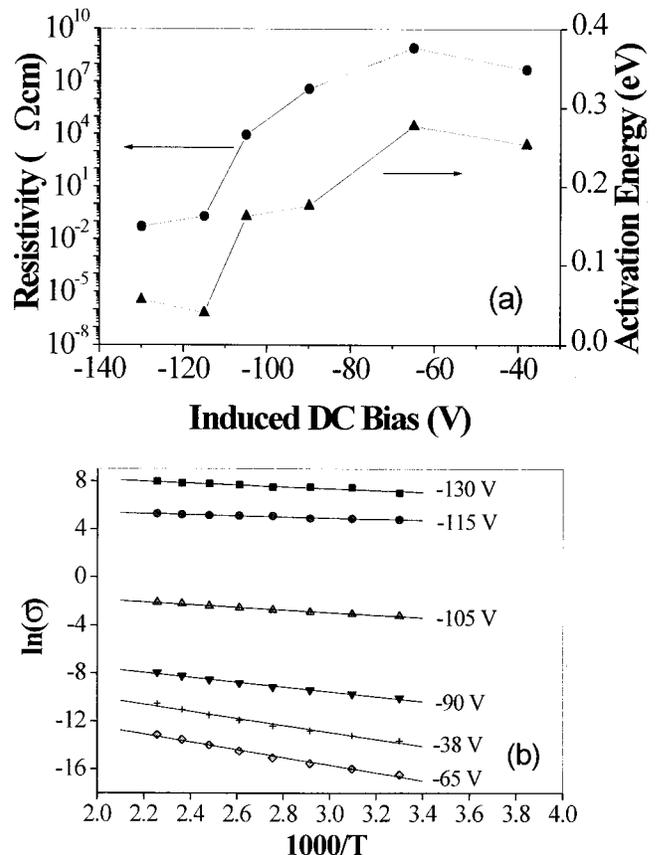


FIG. 4. (a) Resistivity measured using the four point probe technique and the activation energy of the films deposited at different bias voltages. (b) The conductivity of the films measured as a function of temperature.

This type of sharp changes in the resistivity at low metal fraction has also been observed for other Me-C:H films,^{2,8} except that for this series of films, the average Mo/C fraction deduced from RBS with a maximum of only 4%, is comparatively much lower. Nevertheless, in interpreting these results, it should be cautioned that the Mo fraction is not uniform across the depth of the samples as can be seen in Fig. 2. Moreover, there tends to be abundant oxygen atoms incorporated on the surface of the films at low and high dc bias voltages, as indicated in Table I, that can affect the conductivity measured.¹² These Mo-C:H films are rather reactive to oxygen, which could react with Mo to form metal oxide, or with carbon atoms to form C-O or C=O bonds, particularly near the surface attributed to postdeposition oxidation.¹² The presence of oxygen in the films can result in a higher resistivity, particularly if substantial amount of the oxygen atoms is bonded to the Mo. Therefore, oxygen will affect the actual value of the resistivity. This is expected in samples deposited at -130, -65, and -38 V where there are substantially higher oxygen contents compared to the other films. For those samples deposited at -115, -105, and -90 V having a two-layer structure, a higher O/Mo ratio is being found in the first layer as compared to the second layer (see Table I). This surface layer is expected to affect the overall resistivity measured using the four-point probe technique.

The conductivity of the films was also studied over a temperature range from 303 to 450 K with the results shown in Fig. 4(b). As these films were deposited at room temperature, higher temperature measurements were not carried out as it had been shown to lead to irreversible conductivity changes, which could be a result of structural changes caused by increased oxidation (metal-oxide) in these films, dehydrogenation and graphitization of the hydrocarbon matrix. An attempt was made to model the conductivity in the simplest form, namely $\sigma = \sigma_0 \exp(-E_a/kT)$, assuming temperature independent prefactor σ_0 and activation energy E_a . The results are shown by the solid lines in Fig. 4(b), which to a first order reasonably describe the data for all the samples over the range of temperature studied. The activation energies deduced are shown in Fig. 4(a). The modeling allows us to obtain a measure of the degree of thermal activation in the conductivity at different Mo fractions. It should not be taken as indicating any prevailing conduction behavior in these films as the temperature range studied is not wide enough. The activation energy shown in Fig. 4(a) clearly reveals a thermally activated conductivity for samples with low Mo fraction, as is common for amorphous semiconductors like pure DLC films. A decrease in the dependence of the conductivity on temperature at higher Mo fraction suggests an enhanced metallic conduction in these films. A detailed study of the conduction mechanism in these films is in progress.

Tauc gaps (τ_c) deduced for these films deposited on glass substrates, using a Perkin-Elmer Lambda 16 dual beam spectrophotometer, are shown in Fig. 5. The optical data of all the samples were interpreted using a single layer optical model, ignoring the two-layer structure found in three of the samples. Nevertheless, from the large change in the optical gap observed, the trend seen for τ_c should not be critically affected by the simplified model. Consistent with

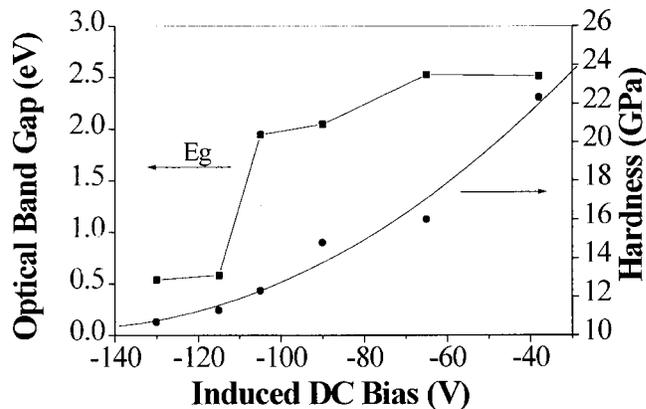


FIG. 5. The Tauc gap (τ_c) and the hardness of the films deposited at different bias voltages.

the resistivity results, two plateau regions are observed, one at the lower while the other at the higher dc bias range. Moreover the sharp transition region in the resistivity change over the dc bias range from -105 to -115 V is also observed in the optical gap variation. This indicates a strong correlation between the electrical and optical properties of these films, a result that was also observed for the W-C:H films studied.⁸

The hardness of the films measured using the Nanoincenter II system are shown in Fig. 5, where a decrease in the hardness can be seen at increasing dc bias. Our previous studies on W-C:H films with W fraction less than 8% exhibited constant hardness when the dc bias voltages at the substrates were held constant.⁸ This was attributed to the fact that the W fraction incorporated was small such that the mechanical properties of the films were still predominantly controlled by the a-C:H matrix. A separate study on another series of Mo-C:H films deposited at constant substrate bias similarly revealed that the hardness was independent of the Mo incorporation for small Mo fraction. However, as the Mo fraction exceeded certain threshold value, a monotonous increase in the hardness attributed to the formation of Mo carbides in these films was observed.⁹ Interestingly, a similar trend was also observed in the case of Ti-C:H films, with the Ti threshold of about 15 at.%.⁴ Therefore, the low level of Mo fraction incorporated into the Mo-C:H films grown for this study was not expected to influence the film hardness. The present result of reduced hardness at larger bias voltages, which amorphizes the films and promotes the growth of sp^2 bonded carbon. The proposed structural change is supported by the Raman results to be discussed shortly, and has also been observed for pure a-C:H films deposited using the present system.¹³ It has been shown that there exists an optimum ion energy for achieving maximum hardness in a-C:H films, beyond which the hardness decreases with the bias voltage.^{13,14} The present results may suggest that the bias voltage range used in this study has already exceeded the optimum energy for the deposition of Mo-C:H films. In considering the optimum energy, it should be noted that the mass of the bombarding ions must also be taken into account.

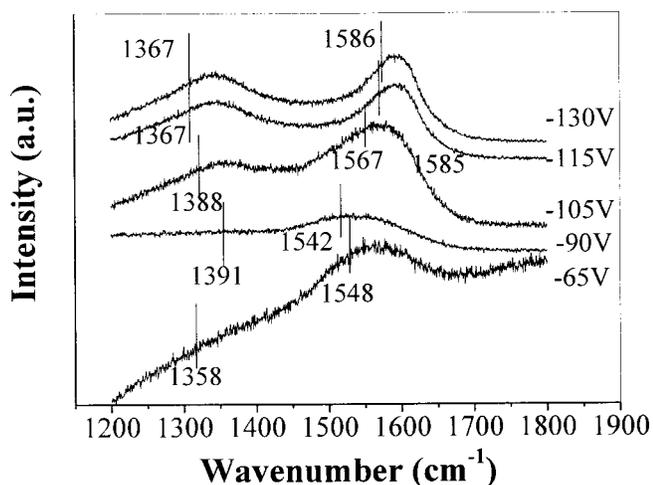


FIG. 6. Raman scattering of the films deposited at different bias voltages.

Raman scattering of the films excited by an Ar^+ laser at 514.5 nm was measured using the SPEX1400 system. The G peak at around 1570 cm^{-1} typical of $a\text{-C:H}$ films can be clearly seen from the results shown in Fig. 6, and is evident of the amorphous structure of these films. Crucial to the present study is the increase in the intensity of the D peak (around 1367 cm^{-1}), attributed to the disorder activated optical zone-edge phonons, relative to that of the G peak. A larger ratio of the integrated intensity of the D peak to G peak has been shown to be correlated to an increase in the sp^2/sp^3 bonded carbon in DLC films.¹⁵ Assuming that the Raman scattering of the Mo-C:H films are derived mainly from the hydrocarbon matrix, the results showing an increase in the sp^2 fraction in the films at higher Mo fraction are therefore correlated to the decrease in the hardness of the films observed. This is consistent with the earlier discussion that the mechanical properties of the films should still be mainly determined by the structures of the amorphous carbon network at low level of Mo incorporated.

IV. DISCUSSION

By incorporating two screen grids, the ECR-CVD system has been successfully applied for the deposition of Mo-C:H films. The technique is unique as it provides flexibility in controlling several crucial growth parameters, and the advantages that accompany a highly ionized ECR plasma.⁸ The increase in the Mo fraction in the films despite the constant Mo sputtering rate can be accounted for by the creation of Mo^+ ions due to ionization by energetic electrons in the ECR plasma. As the grids were biased at -330 V and the substrate holder at -38 to -130 V , there is a decreasing decelerating field at increasing (more negative) dc bias voltages. Therefore, it is expected that the ion energies of the various species, including that of Mo^+ , increase with the dc bias voltage and hence lead to a larger fraction of Mo in the films. Besides being implanted into the films, the Mo^+ ions are also expected to play a significant role, in addition to the Ar^+ ions, in modifying the structures of these films through energetic bombardment at the surface of the growing films. The results obtained suggest that these ions predominantly

amorphized these films through energetic impact. The contribution by Mo^+ ions can be very significant as a result of their larger mass, and can possibly explain the decrease in the hardness of the films observed even at low dc bias voltages.

The decrease in resistivity at higher dc bias voltages is certainly related to the presence of Mo in the films. Taking a closer look at Table I, it can be seen that at the lower bias voltages of -38 and -65 V , Mo appears close to the film surface. As the bias voltage is increased to -90 V , the surface O and Mo fractions are observed to decrease, possibly a sputtering effect. Mo is detected about 80 nm below the film surface. The oxygen contents of these films deposited at intermediate bias voltages are relatively low compared to those grown at substrate bias of -38 , -65 , and -130 V . The slow increase in average Mo from 0.0132 to 0.032 cannot explain a sudden drop of 9 orders of magnitude in resistivity for films grown at -90 , -105 , and -115 V . The observed drop in resistivity for these films is likely to be due to a microstructural transition in the films. The impinging Mo ions could be energetic enough to be implanted into the deeper layer of the films as the substrate bias voltage is increased. This can result in the formation of large Mo clusters for a Mo/C fraction of 0.0624 as indicated in Table I (or 5.8 at. % Mo), at about 114 nm below film surface for the sample deposited at -115 V . At -130 V , the resistivity of the film reaches a plateau, and the oxygen content increases to about 15%. New species of Mo oxides instead of Mo clusters could have formed at the high bias voltage. A similar behavior in the optical band gap for increasing bias voltage has been observed. Clearly, the energy of the bombarding Mo ions does critically affect the composition and the microstructure of the films, leading to the large conductivity observed. In addition, for samples exhibiting two distinct layers with a higher ratio of O/Mo found at the surface, the conductivity measured could be affected.

Structural changes in the amorphous carbon matrix at increasing bias voltages, mainly an increase in the carbon sp^2/sp^3 ratio as deduced from the Raman results, could have also in some ways modified the resistivity of these films.³ Their contribution is expected to be significant when the atomic fraction of metal involved is small. However, it is not likely that this alone could account for the large resistivity change observed. In our experiment, it was also noted that the Mo fraction incorporated was dependent on the type of substrate used. Samples deposited on glass generally tend to contain slightly larger metal fractions, as was evident from their more metallic appearance, especially for films incorporated with higher levels of Mo. Since the conductivity was measured using the four point probe technique for films deposited on glass substrates, whereas the atomic fractions were determined by RBS for films deposited on Si substrates, therefore the large conductivity observed at the relatively low level of Mo incorporated could be partly accounted for. No conductivity measurement was performed for films deposited on Si substrate [n -doped (100), 0.01–0.02 $\Omega\text{ cm}$] as the relatively conductive substrate itself can distort the conductivity measured. As such, we were not able to exactly compare the conductivity of the same films deposited

on different substrates. Nevertheless, it is believed that the substrates used, glass and crystalline Si, will to a certain extent determine the properties of the films deposited. This is particular so as the two substrates have quite different conductivities, and the more insulating glass substrate will be likely to experience charge built-up on the growing film surface, resulting in the shielding of the applied bias voltage. This will influence the impinging ion energy and hence the properties of the films deposited. A detailed study on the electrical conduction mechanism in these films, a work that is in progress, will be able to further shed light on the exact cause for the large change in conductivity observed.

From the activation energy results, it is proposed that the structures of the Mo–C:H films investigated are dominated by the presence of Mo clusters embedded within an amorphous carbon matrix. Intercluster tunneling of electrons is responsible for the thermally activated conduction behavior observed for samples with lower Mo fractions deposited at low bias voltages. With increasing Mo fraction, microstructural changes as a result of energetic ion bombardment as well as formation of large Mo clusters account for the extremely low resistivity observed.

V. CONCLUSION

Mo–C:H films deposited using a technique based on an ECR-CVD system in conjunction with two biased screen grids have been investigated. The fraction of Mo incorporated was noted to increase with the dc bias applied at the substrates. The resistivity and hardness of the films were correspondingly found to decrease sharply. At the present level of Mo inclusion, the mechanical properties of the films

are predominantly determined by the microstructures of the amorphous hydrocarbon network, which in turn are determined by the energy of the impinging ions through the applied bias at the substrates. The ion energy is also noted to critically affect the composition and the microstructure of the films, leading to the large conductivity observed.

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