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Electrical properties of a-C:Mo films produced by dual-cathode filtered cathodic arc plasma deposition

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Abstract

Molybdenum-containing amorphous carbon (a-C:Mo) thin films were prepared using a dual-cathode filtered cathodic arc plasma source with a molybdenum and a carbon (graphite) cathode. The Mo content in the films was controlled by varying the deposition pulse ratio of Mo and C. Film sheet resistance was measured *in situ* at process temperature, which was close to room temperature, as well as *ex situ* as a function of temperature (300-515 K) in ambient air. Film resistivity and electrical activation energy were derived for different Mo and C ratios and substrate bias. Film thickness was in the range 8-28 nm. Film resistivity varied from $3.55 \times 10^{-4} \Omega \text{ m}$ to $2.27 \times 10^{-6} \Omega \text{ m}$ when the Mo/C pulse ratio was increased from 0.05 to 0.4, with no substrate bias applied. With carbon-selective bias, the film resistivity was in the range of 4.59×10^{-2} and $4.05 \Omega \text{ m}$ at a Mo/C pulse ratio of 0.05. The electrical activation energy decreased from 3.80×10^{-2} to 3.36×10^{-4} eV when the Mo/C pulse ratio was increased in the absence of bias, and from 0.19 to 0.14 eV for carbon-selective bias conditions. The resistivity of the film shifts systematically with the amounts of Mo and upon application of substrate bias voltage. The intensity ratio of the Raman D-peak and G-peak (I_D/I_G) correlated with the pre-exponential factor (σ_0) which included charge carrier density and density of states.

Keywords: metal doped amorphous carbon, electrical properties, cathodic arc deposition, Raman spectroscopy.

1. Introduction

Thin films of metal-doped diamond-like carbon (Me-DLC) are of interest for their properties of good adhesion [1], high hardness [2], low friction coefficient [3], high thermal stability [4] and high electrical conductivity [5]. The electrical conductivity of the film varies with the amount of the incorporated metal [6, 7]. Several techniques have been used to deposit metal-doped DLC films, including a metal cathodic arc in acetylene [8] and cathodic arc deposition [9]. Almost all deposition techniques involve some hydrocarbon gas.

In this paper, we report on the deposition of molybdenum-containing amorphous carbon (a-C:Mo) thin films using a dual-cathode filtered cathodic arc plasma source with a molybdenum cathode as the metal source and a graphite cathode as the carbon source. There are no process gases involved. One objective of this research is to fabricate thin films for applications at room temperature where hard *and* conducting films are needed. Another objective is to contribute to an understanding of conductivity and structure of molybdenum doped a-C films.

The experiments were carried out with different arc pulse ratios of molybdenum and carbon, and different carbon-selective bias voltages. Film sheet resistances were measured during deposition. Electrical activation energies were determined *ex situ*, and the films were further characterized by Raman spectroscopy.

2. Experimental details

Si (100) wafers and microscope boron silicate glass slides with sputtered molybdenum contacts were used as the substrate materials. The electrical contacts were made on two terminal of the glass slide, leaving a center square area of 25 mm x 25 mm for film deposition [10]. The sheet resistance was continuously recorded using the two-terminal configuration. It was important to use the same metal for contacts as was used for doping to minimize the contact effects. The a-C:Mo films were deposited by the pulsed dual-cathode filtered cathodic arc plasma source system shown in Fig. 1.

The pulsed cathodic arc source has two cathodes in one anode body [11], representing a modified “minigun” [12]. The cathodes are pulsed using the “triggerless” arc initiation method [13]. The streaming plasma was guided and transported through a curved magnetic macroparticle filter [14] into the magnetic plasma homogenizer [15, 16] to deposit high-quality films.

The cathodes were 6.4 mm diameter rods, separated by 2 cm centre to centre distance. The cathode spots burned on the front face only, the rest of the cathode surface was enclosed

by alumina ceramic. The plasma from both cathodes entered the same macroparticle filter. The 90-degree bent filter coil was made of copper tubing with 22 turns, 7 cm in diameter. The filter magnetic field was generated by the arc current utilizing a series circuit for arc and filter. Two separate power supplies were used for this experiment, one for Mo and one for C [17]. The arc pulse length and current amplitude were 5 ms and 120 A for C, and 1 ms and 760 A for Mo, respectively.

The magnetic plasma homogenizer was a magnetic multipole with 16.7 cm inner diameter; its function is to improve film uniformity. The distance between the exit of the curved filter to the homogenizer was 2 cm, and distance from the magnetic homogenizer to the substrate was 2 cm. The vacuum base pressure was about 0.3 mPa; no process gas was used. The pulse repetition rate was 2 pulses per second. The *in situ* film sheet resistance was monitored using a FLUKE 189 digital multimeter connected to a computerized data acquisition system. Film resistivity was determined from the sheet resistance, R_{\square} , according to $\rho = R_{\square}d$, where d is the film thickness. The thickness was calibrated using by profilometry and assuming that the deposition rate per pulse is constant, i.e., pulse counting is sufficient to determine the thickness of ultrathin films.

Two kinds of experiments were done. First, we varied the Mo/C pulse ratio without substrate bias. Second, the films were deposited at constant pulse ratio of Mo/C=0.05 and varied pulsed substrate bias voltage from -100 V to -1000 V, *applied to carbon only*. This could be achieved by the computerized synchronization of carbon pulses and bias power supply, which we call species-selective bias. The negative bias voltage was pulse with 25% duty cycle (4 μ s on, 12 μ s off). The total deposition pulse number was 2000 pulses for each film. The substrates were cleaned by ethyl alcohol and dried with a flow of pure dry nitrogen before mounting on the substrate holder. For deposition run, a witness sample of Si (100) wafer was used for profilometry, and another witness sample of borosilicate glass to be used for Raman spectroscopy.

After film deposition, the samples were left in ambient air at room temperature. Their sheet resistances were record weekly for two months to determine the stability of the films. After this period, temperature dependent measurements of the film sheet resistances were carried out in the range 300 to 515 K in ambient air. A K-type thermocouple was placed at the back of the sample to determine the temperature. Both temperature and sheet resistance were recorded during heating by FLUKE 189 digital multimeter.

The resistivity measurements (via measurements of sheet resistance and film thickness) were complimented with visible Raman spectroscopy, which would allow us to approximately deduce sp^2/sp^3 ratio and to make tentative conclusions on the conduction mechanisms. The Raman spectroscopy was done with the 514 nm line of an argon ion laser.

3. Results and discussion

Fig. 2(a) shows the resistivity change during film deposition at a constant Mo/C pulse ratio of 0.05. The maximum resistivity in the absence of bias was recorded at $1.25 \Omega \text{ m}$ and reduced to $3.38 \times 10^{-4} \Omega \text{ m}$ at the end of deposition. For carbon-selective bias with -100 V pulsed, the maximum resistivity was $3.23 \Omega \text{ m}$, and reduced to $1.34 \Omega \text{ m}$ at the end of deposition (Fig. 2(b)).

The film resistivity was changing in the same manner for other Mo/C ratios and other bias voltages. The inset in Fig. 2 show the results of films resistivity measured two months after deposited for films with different Mo/C ratios (a) and different bias voltages (b). The corresponding resistivity was $3.55 \times 10^{-4} \Omega \text{ m}$ maximum and $2.27 \times 10^{-6} \Omega \text{ m}$ minimum in the absence of bias. For carbon-selective bias at the constant Mo/C pulse ratio of 0.05, the resistivity had a maximum of $4.05 \Omega \text{ m}$ maximum at -200 V bias and a minimum of $4.59 \times 10^{-2} \Omega \text{ m}$ at -1000 V bias. The film thickness was in the range 8-13 nm without bias and between 21-28 nm for carbon selective bias. These results indicate that film resistivity is affected by both Mo content and bias voltage.

Although the exact conduction mechanism of metal-containing amorphous carbon films remains unclear, it is generally believed that the introduction of metal into the amorphous carbon films will increase the complexity of the electronic transport properties which is mainly controlled by sp^2 clusters. Huang et al. [7] have reported that there are two types of conduction mechanisms in molybdenum-containing diamond-like carbon films; thermal activation and tunneling coexist, and they dominate the conduction behavior in the high and low temperature regimes, respectively. They found that a conductivity turning point around 115 K. Above the turning point, the electrical conductivity, σ , of the film can be written as an exponential function of temperature, T, in the form

$$\sigma(T) = \sigma_0 \exp (-E_A/k_B T) \quad (1)$$

where E_A is the activation energy for electric conduction, σ_0 is the pre-exponential factor determines by the charge carrier mobility and density of states, and k_B is the Boltzmann

constant. Since we operated above room temperature in our tests, the application of this equation is well justified.

Fig. 3 shows an Arrhenius plot of the reciprocal temperature and $\ln(\sigma)$ obtained from the temperature dependent sheet resistance measurement. In our temperature test range, the film conductivity followed equation (1). Equation (1) shows a linear relationship between $\ln(\sigma)$ and the reciprocal of temperature. A linear fit was taken to determine the activation energy and the pre-exponential factor for the temperature range 300-515 K. The results are shown in Fig. 4.

There is a trend for the activation energy to decrease with increasing molybdenum content while the pre-exponential factor increases. For carbon selective bias at the constant 0.05 Mo/C pulse ratio, the activation energy decreases with increasing negative bias voltage and the pre-exponential factor increases. The calculated σ_0 values for the film prepared for a pulse ratio of $0.05 < \text{Mo/C} < 0.4$ without bias were in the range of 10^4 - $10^5 \Omega^{-1} \text{ m}^{-1}$, and less than $10^4 \Omega^{-1} \text{ m}^{-1}$ for various substrate bias at 0.05 Mo/C pulse ratio.

The Raman spectra (over the range of 900-2000 cm^{-1}) of the films that are prepared with various Mo/C ratios and bias voltages are given in Fig. 5. The spectra exhibit a broad Raman peak in the range of 1000-1700 cm^{-1} . The peak at approximately 1090 cm^{-1} is from the SiO_2 glass substrate. The Raman spectra were fitted with three Gaussian peaks of SiO_2 , and disorder ('D') and graphite ('G') peaks. The peak intensity ratio (I_D/I_G) plotted as a function of Mo/C and bias voltage are given in Fig. 6. It can be seen that the I_D/I_G ratio increases with increasing Mo/C ratio (a). Looking at the influence of substrate bias on the intensity ratio of I_D/I_G , one can see that I_D/I_G decreases slightly from an initial value of 0.36, reaches a minimum at approximately between 300-400 V bias voltage, and then increases rapidly (b). We quote applied bias voltage, however, one should note that the actual potential on the glass slide surface is not exactly the applied bias voltage, which is applied to the holder, rather, a time-dependent voltage drop appears between holder and substrate surface. Since the actual surface potential is not well known, we use the applied voltage. The I_D/I_G ratio is an indication of sp^2 to sp^3 bonds in the deposited films [18]. It can be observed that the I_D/I_G ratio has a trend that correlates with the pre-exponential factor σ_0 shown in Fig. 4. This can be explained by an increase in the conductive pathways caused by an increase in the fraction of conductive graphite-like material. However, the varying trends of I_D/I_G ratio of a-C:Mo films with substrate bias are the same as that of the pure ta-C [19] and ta-C:W films [20].

In addition to the above arguments one may consider whether or not Mo clustering and percolation of Mo clusters could contribute to the conduction mechanism. As long as the Mo concentration is low, there is reason to believe that this is not the case because Mo atoms will be relatively even distributed and cannot diffuse to form clusters. Monte Carlo TRIM simulation of the subplantation process shows that the molybdenum ions from the plasma are energetic enough to penetrate the surface the growing film due their relatively kinetic energy of about 150 eV [A. Anders and G. Y. Yushkov, J. Appl. Phys., vol. 91, pp. 4824-4832, 2002]. TRIM shows that 150 eV Mo ion have a projected range of about 1.2 nm. The small collision cascades such ions caused are quenched on a timescale of about 1 ps or less, that is, the Mo atom has found a "resting place" and has become immobilized by having formed bonds to neighboring carbon atoms. At high molybdenum concentrations, it is conceivable that clusters of Mo form. The dependence of the resistivity on the selective bias, *applied to carbon only*, shows that the energy dependent formation of a-C material, characterized by its sp^2/sp^3 ratio, has a dramatic effect on the conductivity. Presence and clustering of sp^2 seems therefore indeed a key feature for conducting hard carbon films. This is perhaps the main result and conclusion of the present work.

4. Conclusion

Molybdenum-containing amorphous carbon (a-C:Mo) films have been synthesized using a dual-cathode filtered cathodic arc plasma deposition. The experiment results show that both the amount of Mo contained in a-C:Mo films and the bias voltage acting on carbon ions during growth can affect the film resistivity. The sp^2 fraction in the films correlated with electrical conductivity of the films. The film thickness can be controlled by the numbers of deposition pulses and the film resistivity by the Mo/C ratio and bias voltage. This technique can produce ultrathin films that combine properties of hard carbon and a certain conductivity at room temperature that is much higher than for undoped a-C.

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Figure Captions

Fig. 1. Schematic diagram of the pulsed dual-cathode filtered cathodic arc plasma system.

Fig. 2. Film resistivity during deposition process with a Mo/C pulse ratio of 0.05 (a) without bias and (b) with carbon-selective bias at -100 V.

The insets show the resistivity two month after deposited of various Mo/C deposition pulse without bias (a) and of various carbon selective bias voltage at constant Mo/C deposition pulse of 0.05 (b).

Fig. 3. Arrhenius plot of the film conductivity at (a) various Mo/C deposition pulse ratio without bias and (b) under different substrate bias voltage at constant Mo/C deposition pulse ratio of 0.05.

Fig. 4. Electrical activation energy and pre-exponential factor of a-C:Mo film deposited at (a) different Mo/C deposition pulse ratios without bias and (b) different carbon selective bias voltages at constant Mo/C deposition pulse ratio of 0.05.

Fig. 5. Raman spectra of the a-C:Mo films prepared at (a) various Mo/C deposition pulse ratios without bias and (b) various bias voltages at constant Mo/C deposition pulse ratio of 0.05 .

Fig. 6 Variation of the Raman intensity ratio, D and G peaks, as a function of (a) various Mo/C deposition pulse ratios without bias and (b) various carbon selective bias voltages at constant Mo/C deposition ratio of 0.05.

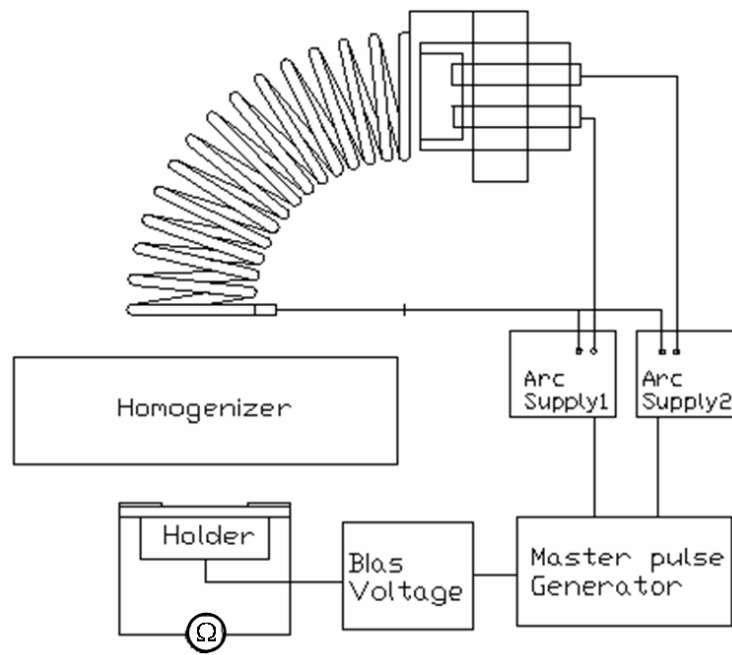


Fig. 1

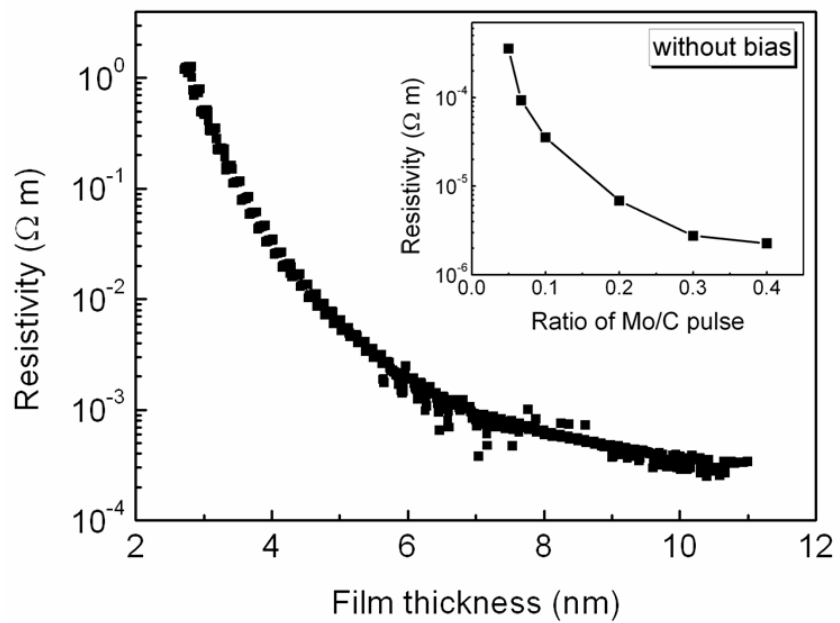


Fig. 2(a)

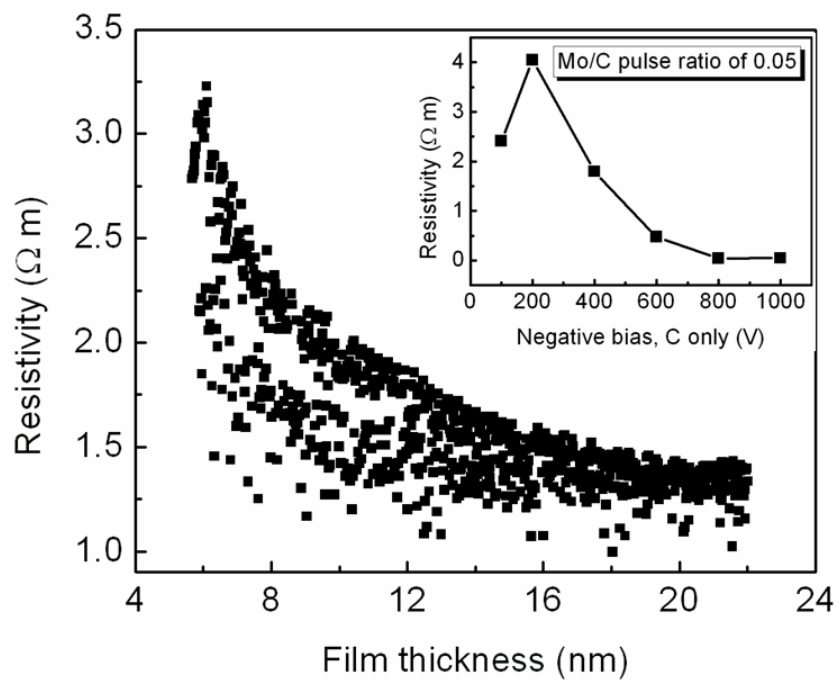


Fig. 2(b)

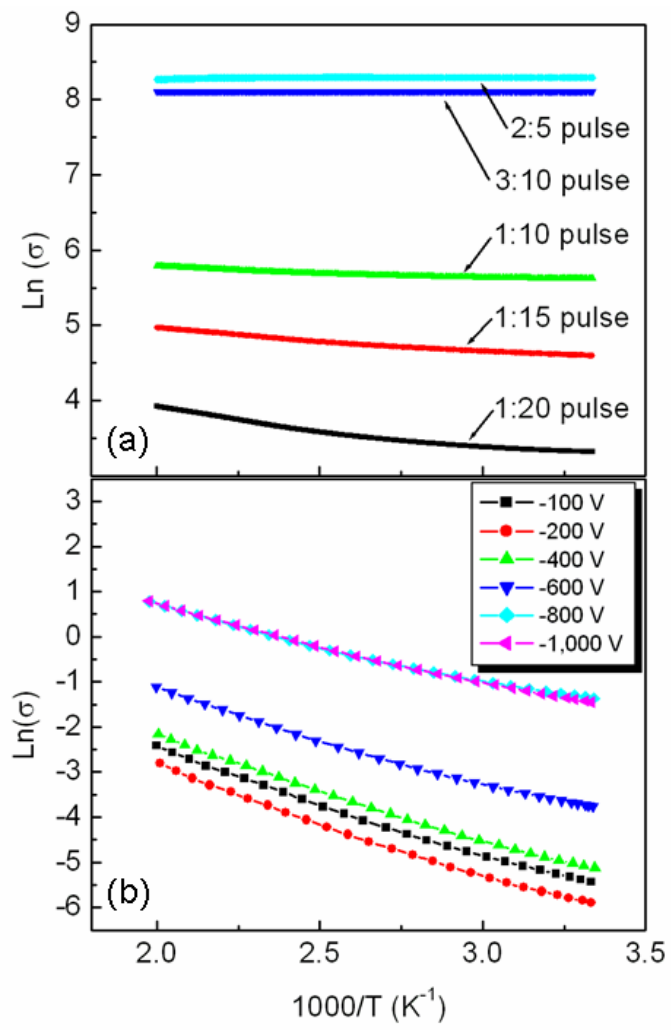


Fig. 3

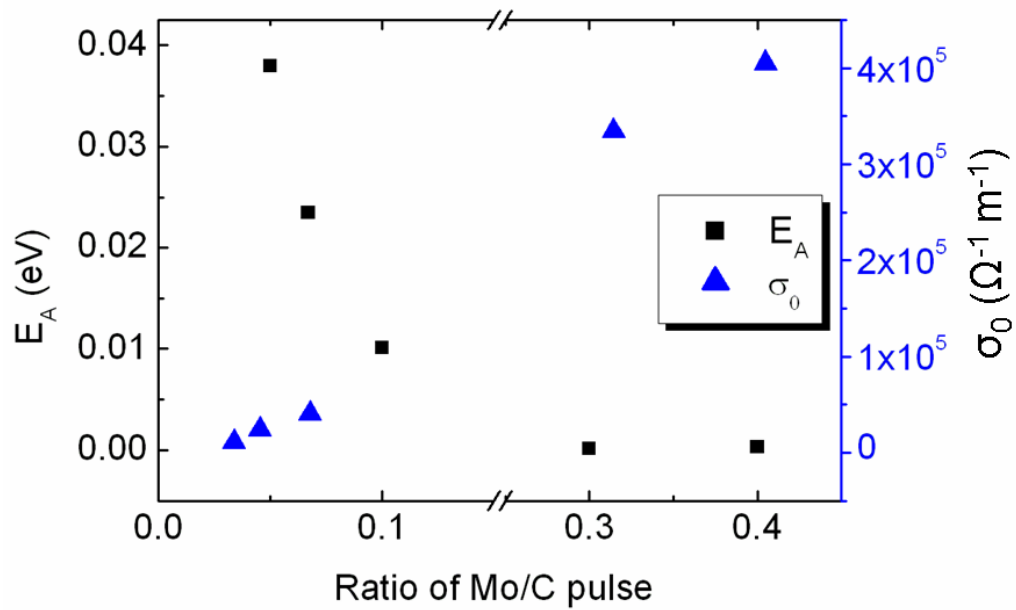


Fig. 4(a)

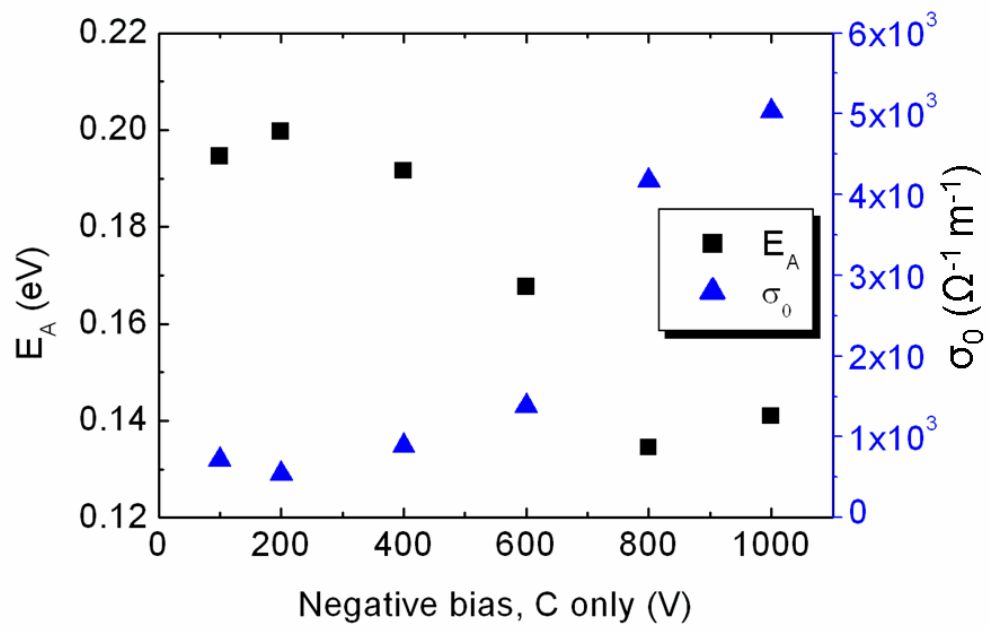


Fig. 4(b)

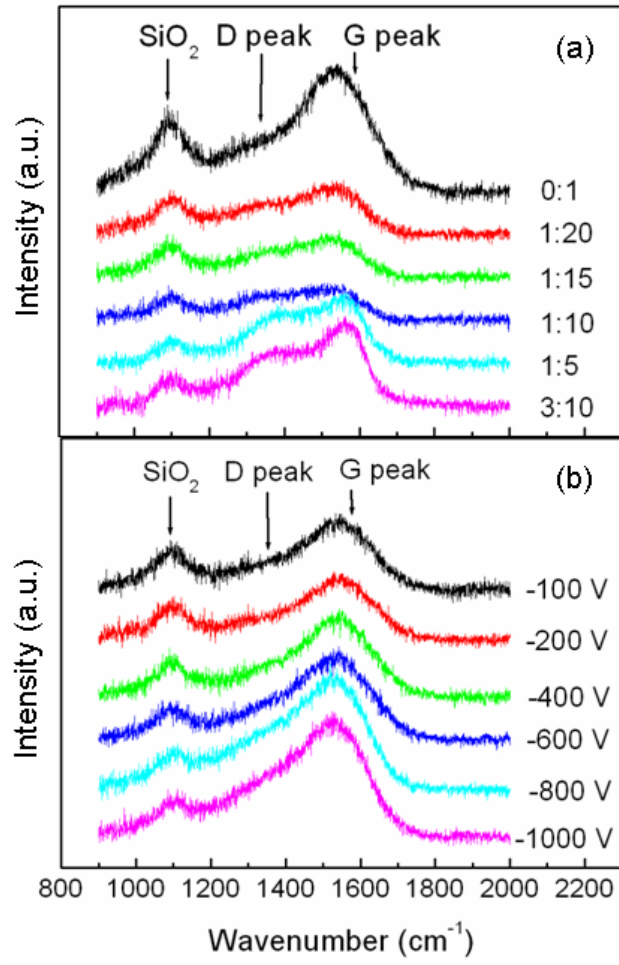


Fig. 5

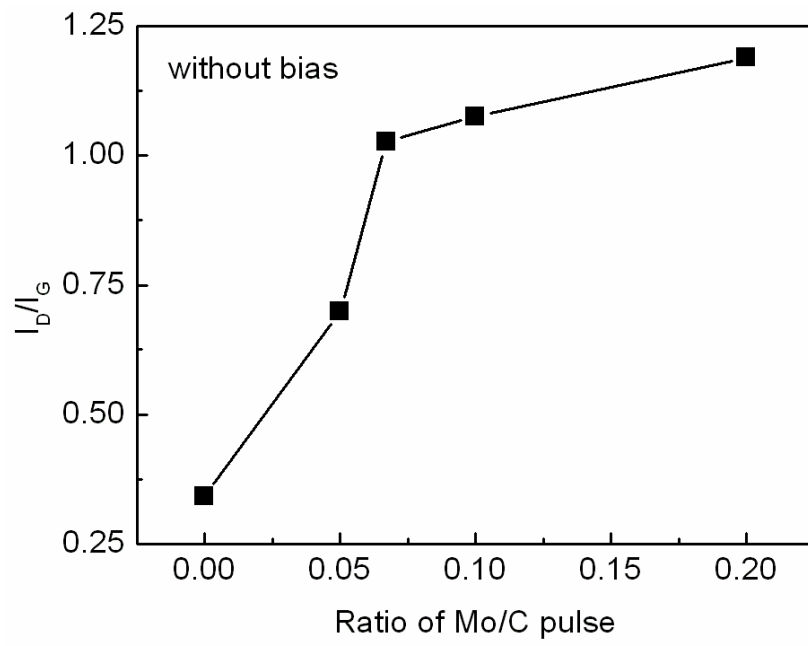


Fig. 6(a)

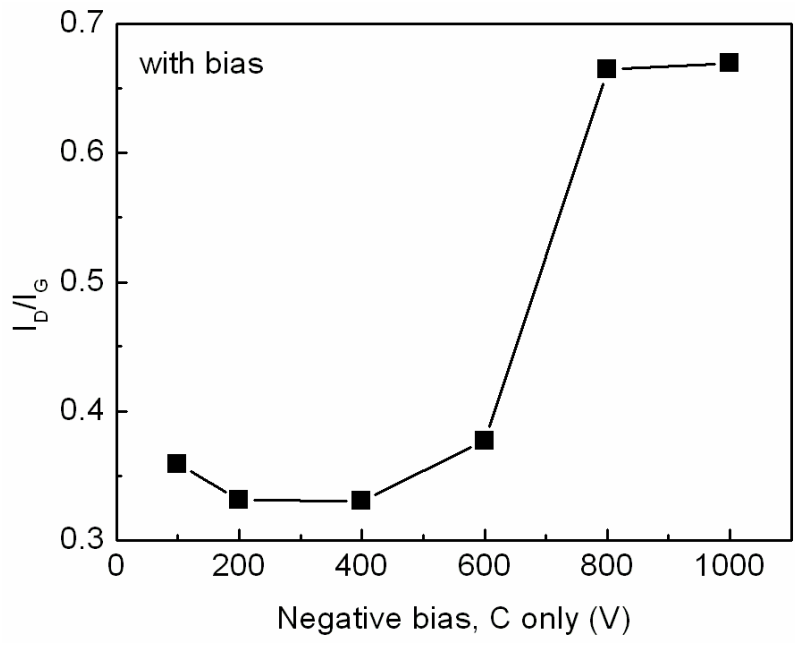


Fig. 6(b)