

# Characteristics of Cu/C films on polymer substrates prepared by ECR–MOCVD

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**Abstract** Cu/C films were prepared at ambient temperature under a  $\text{Cu}(\text{hfac})_2\text{-Ar-H}_2$  atmosphere in order to obtain metallized polymer by using electron cyclotron resonance metal organic chemical vapor deposition (ECR–MOCVD) coupled with a direct current (DC) bias system. DC bias selectively attracts the positively charged copper ions and then makes them deposit on the polymer substrate. Structural analysis of the films by ECR showed that fine copper grains were embedded in an amorphous polymer matrix. The electrical properties of the films were closely related to the process parameters such as microwave power, magnet current,  $\text{H}_2/\text{Ar}$  mole ratio and periodic negative voltage. The increase in  $\text{H}_2$  contents, microwave power, magnet current and the negative voltage brought on copper-rich film formation with low electrical resistance. On the other hand carbon-rich films with low sheet electrical resistance were prepared with lower values for process parameters described above. Formation of Cu/C films depends strongly on the periodic negative pattern of DC bias and the electrical sheet resistance of the films was controlled in the  $10^8\text{--}10^0$  ohm/sq range by process parameters of the ECR–MOCVD system.

## Introduction

Metal composites in the form of thin films on a plastic substrate are very interesting materials for microelec-

tronic packaging [1] and for electromagnetic interference (EMI) shielding [2]. Copper is especially very attractive for conductors due to its high electrical conductivity and electro migration resistance. For many of these applications, adhesion of most metallic materials to the polymer and film preparation at low temperature, especially at room temperature, are critical [3, 4].

Conventional methods for metallization of polymer are electroless plating and physical vapor deposition (PVD) such as thermal evaporation and sputtering. In addition to these conventional techniques, ion-beam-assisted deposition (IBAD) can also be used. Wet chemistry processes, however, have some inherent problems such as complex procedures and environmental pollution. For the vacuum deposition, it is technically difficult to maintain a metal film on the polymer substrate due to poor adhesion, substrate deformation and an aging effect [5, 6].

CVD processes for the preparation of copper films are of considerable interest since continuous deposition of large areas can be easily achieved with good film characteristics. Most established metal organic chemical vapor deposition (MOCVD) techniques for the preparation of copper film are based on thermal CVD procedures. Operating temperatures in the range of 150–200 °C have to be used to prepare copper thin films by plasma enhanced chemical vapor deposition (PECVD) [7, 8]. Deposition of thin copper film on polymer substrates by the MOCVD method at room temperature has not been tried.

The present paper concerns the preparation of thin copper films on polymer substrates at room temperature by means of ECR–CVD procedures. The ECR–CVD method has attracted much attention for its high

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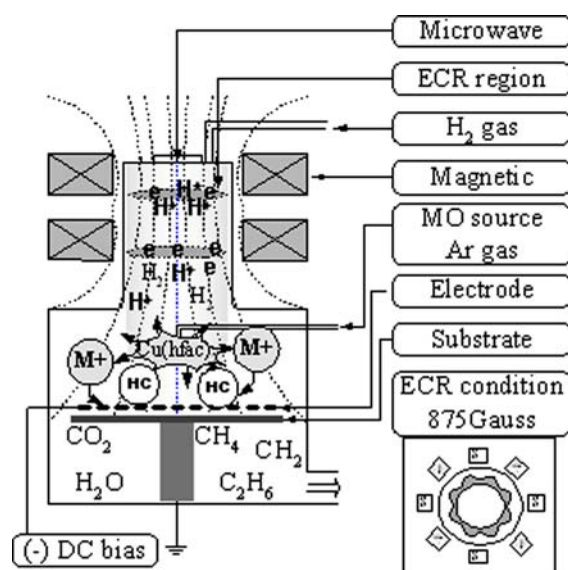
electron density of  $10^{17}$ – $10^{18}$   $\text{m}^{-3}$  at a gas pressure range of  $1 \times 10^{-4}$  to  $5 \times 10^{-3}$  torr [9, 10]. Enhancement of ionization can be obtained by ECR plasma. The function of ECR is to increase the path of electrons in the plasma by applying a magnetic field normal to the electron trajectory. Charged electrons or ions from plasma undergo a circulatory motion normal to the direction of the magnetic field. Resonance is achieved when the frequency at which microwave energy is fed to an electron circulating in a magnetic field is equal to the characteristic frequency at which the electron circulates. This circulating motion increases the ratio of ionized to non-ionized species in ECR plasma by three orders of magnitude over that in conventional radio frequency plasma.

Recently, there has been great interest in using MOCVD at ambient temperature in order to produce metallized polymer. Chemical vapor deposition at ambient temperature using organometallic precursors should be possible with the aid of direct current (DC) bias. The periodic negative voltage from DC bias near the substrate induces ions and radicals to nucleate on the surface of the substrate. The high efficiency in exciting the reactants in an ECR plasma coupled with periodic negative voltage from DC bias allows the deposition of films at ambient temperature without thermal activation.

The aim of this work was to test the ECR MOCVD method for deposition at room temperature and characterize the films prepared thereby. We also report the results of experiments designed to investigate the deposition of copper on carbon containing hybrid thin films from  $\text{Cu}(\text{hfac})_2$  as a copper precursor in an  $\text{Ar-H}_2$  atmosphere by using ECR microwave plasma coupled with DC bias. The structural and chemical analyses of the  $\text{Cu/C}$  films were carried out and their electrical resistances were determined as a function of  $\text{H}_2/\text{Ar}$  mole ratio, microwave power, periodic negative voltage and the magnet current.

## Experiment

An Astex-1000 ECR plasma generator, a CVD reactor and a high vacuum system were employed to carry out the experiments. As shown in Fig. 1, ECR system consisted of two chambers, the plasma chamber and the deposition chamber. The gases are introduced through two separate inlets; hydrogen and argon molecules are introduced into the upper plasma chamber and the lower deposition chamber, while organometallic precursor with carrier gas is fed into the lower deposition chamber. The DC bias is



**Fig. 1** ECR plasma MOCVD experimental apparatus

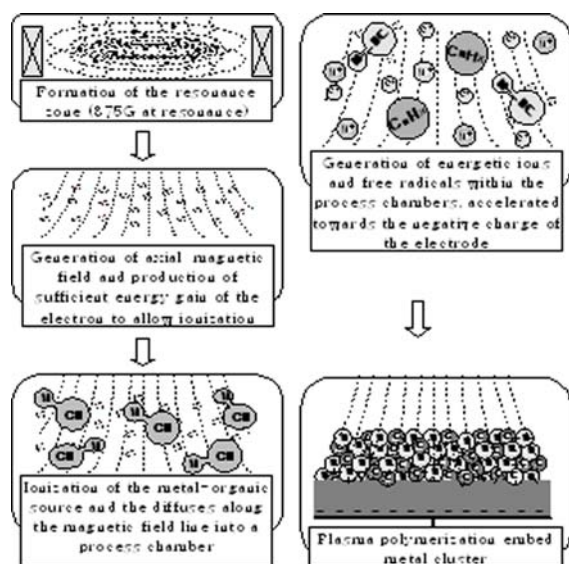
connected to the grid near the substrate, in order to induce metal ion and radicals to form on the surface of non-conductive polymer substrate. The periodic negative voltage pattern was generated by DC bias, which had a maximum voltage of 20 kV and a frequency of 60 Hz.

$\text{Cu}(\text{hfac})_2$  (hfac: 1,1,1,5,5,5-hexafluoro-2,4-pentandione) with purity of 99.9% was employed as a source of copper for the  $\text{Cu/C}$  thin film. The feed rate of  $\text{Cu}(\text{hfac})_2$  was controlled by adjusting the bubbler temperature and carrier gas flow rate through it. Argon was used as a carrier gas and hydrogen gas was fed to the CVD reactor to control the properties of films deposited. Polyethylene terephthalate (PET) sheets were cut into  $5 \times 5$  cm pieces and used as substrates for the deposition of the film. The surface morphology and chemical state of deposited films were examined by scanning electron microscopy (SEM, Hitachi S-4200) and X-ray photoelectron spectroscopy (XPS, PHI 5800), respectively. In addition, the sheet resistance of the deposited film was determined from the current passing through the surface using the four-point probe measurement in a CMT-SR1000N conductivity meter at room temperature.

## Results

### Mechanism of $\text{Cu/C}$ film formation

Figure 2 shows the schematic model of  $\text{Cu/C}$  film deposition by ECR-MOCVD. In the first step, the



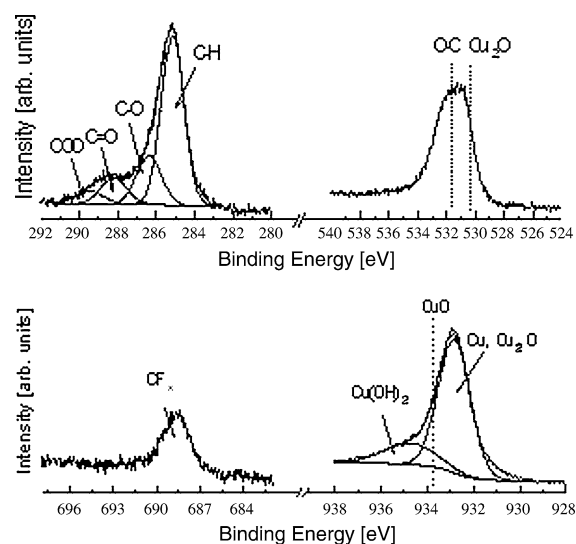
**Fig. 2** Mechanical model of Cu/C film formation

electrons and hydrogen ions with high energy are generated by ion impacts and decomposition of the plasma gas in the ECR plasma zone. After the inelastic collisions of the  $\text{Cu}(\text{hfac})_2$  molecules with electrons and ions, the  $\text{Cu}(\text{hfac})_2$  has been defluorinated and hydrogenated simultaneously. Electrically charged copper ions, carbon clusters, fluorine and hydrogen ions are generated by decomposition of the precursor. Most of Cu ions formed in the bulk plasma are maintained at a positive charge relative to the negatively charged carbon clusters.

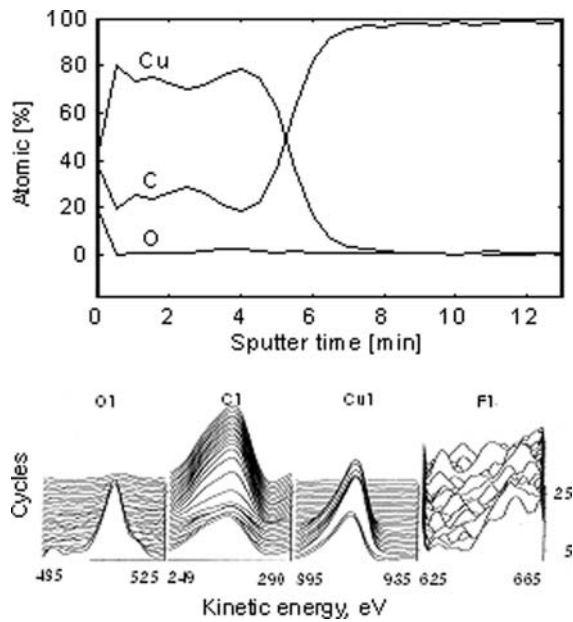
If negative voltage from DC bias did not exist, only reactive hydrocarbon fragments would interact with an activated PET surface and then only the hydrogen enriched polymeric film should be formed. However, when DC bias is coupled with ECR plasma, the periodic negative potential field from the DC bias attracts positively charged copper ions. So, these ions are accelerated toward the electrode causing ion concentrations to abruptly increase around the electrode connected to the DC bias. When copper ion concentration reached a super saturation condition, these condense in the space between the electrode and polymer substrate. The copper nucleates and grows on the surface of polymer substrate because heterogeneous condensation is favored over gas phase homogeneous condensation from the point of view of free energy. Of course, copper deposition on the surface of the electrode also occurred. At the same time, a plasma polymerization reaction proceeds between hydrogen radicals and dangling bonds on the polymer films. As a result, the hydrocarbon matrix is uniformly distributed within the copper films prepared.

### Characteristics of films prepared by ECR-CVD

The chemical state of the film surface prepared by ECR-CVD was analyzed by XPS. The spectra of C1s, O1s, F1s, Cu2p obtained are shown in Fig. 3. Components of the copper precursor,  $\text{Cu}(\text{hfac})_2$ , were incorporated into the surface structure of the films. The C1s spectrum for the copper deposited film by ECR-CVD consisted of four distinct peaks: C–H (285 eV), C–O (286.4–287.0 eV), C=O (288–288.4 eV) and O–C=O (289.1–289.6 eV). The four main peaks are present in a 63.45:19.69:11.18:5.67 ratio as expected based on the dissociation of pentandione groups from  $\text{Cu}(\text{hfac})_2$ . Observing the O1s and F1s spectra, oxidized copper (530.5 eV) and  $\text{CF}_n$  bond (688 eV) were formed. The very small  $\text{CF}_n$  peak indicated that most of the fluorine functional groups in the precursor were converted to volatile hydrogen fluoride by a gas phase substitution reaction with the hydrogen. As a result of curve fitting for the Cu2p spectrum, metal copper (932.7 eV) and CuO,  $\text{Cu}_2\text{O}$  (933.6 eV),  $\text{Cu}(\text{OH})_2$  (935.2 eV) peaks are observed. At the surface an increased amount of oxygen about 20% was attributed to oxidation of the copper film in the atmosphere after the deposition experiments. Figure 4 shows a typical variation of Cu, C and O Auger signals versus sputtering time for the specimen from ECR-CVD. In the specimen of a Cu/C film from ECR-CVD, an AES depth profile shows the formation of a homogeneous Cu/C layer with an average composition of about 80% Cu and 20% C. The content of oxygen in the film was negligible. By observing the chemical shift of the Auger carbon peak



**Fig. 3** (a) C1s, (b) O1s, (c) F1s, (d) Cu2p spectra of Cu/C films prepared by ECR-MOCVD

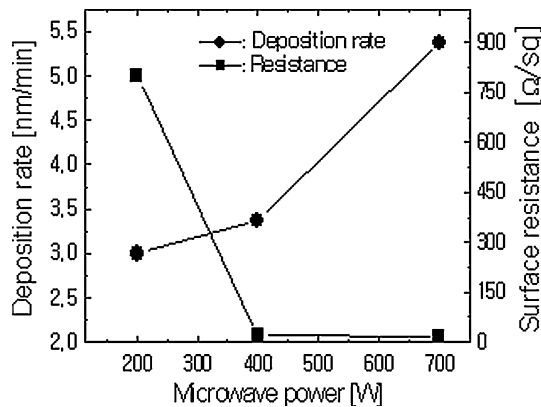


**Fig. 4** AES sputter depth profiles of the Cu/C layer structure prepared by ECR-MOCVD

at the beginning of the profiles in Fig. 4, we can construe that some of the carbon is converted to carbide, possibly due to plasma polymerization during the formation of an organic carbon network in the deposited film.

**Effects of microwave power and magnet current**

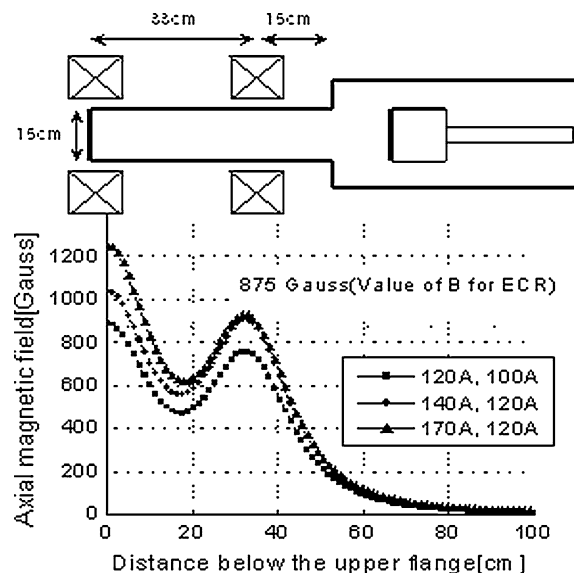
With increase in microwave power, the electrons gain more energy for ionization of molecules, transfer almost all of the electron energy to the molecules during the inelastic collision, and leading to reduction in the electron energy. Thus, the ion density more gradual increased with microwave power and electrons energy simultaneously have stable value [11]. Figure 5 shows the effect of microwave power on deposition rate



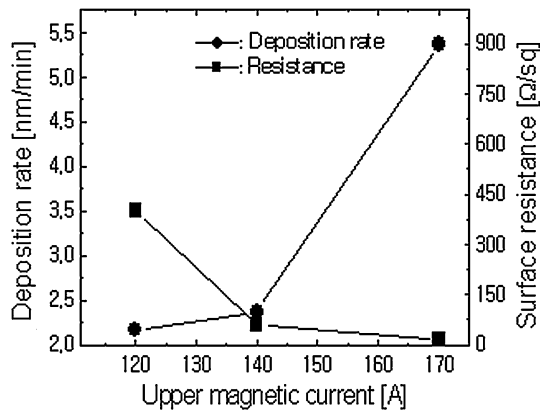
**Fig. 5** Effect of microwave power on deposition rate and electrical resistance of the Cu/C film

and electrical resistance of the film prepared. As shown in the figure, the deposition rate increases with the increase in microwave power, but the electrical resistance sharply decreases above 400 W of microwave power. These results indicate that increasing microwave power gave rise to a higher degree of ionization.

Change in magnet current represents a change in magnetic field intensity. In our ECR system, a magnetic field inside the process chamber is generated using upper and lower electromagnetic coils. Figure 6 show the axial distribution of the magnetic field as a function of the distance below the top flange on the ECR chamber. For the upper magnet operating at 120 A with the lower magnet at 100 A, resonance position with the magnetic field of 875 G has one resonant zone near the top flange on the ECR chamber. In the case of applying the current of the upper and lower electro magnet at 120, 140 A, has one resonant zone near the top flange and two additional zones under the lower magnet. This profile can yield higher ionization efficiencies, due to enhanced confinement of hot electrons that are magnetically trapped between the high field positions [12]. In this work, the upper electric magnet current was changed in order to investigate the effect of magnetic intensity on deposition rate and electrical resistance at a fixed lower electric magnet current of 120 A. As shown in Fig. 7, the deposition rate increases with upper magnet current, but electrical resistance decreases. Therefore, an increase of magnet current brings on an increase of ionization because magnetic intensity increases the electron path and raises the possibility of inelastic collisions.



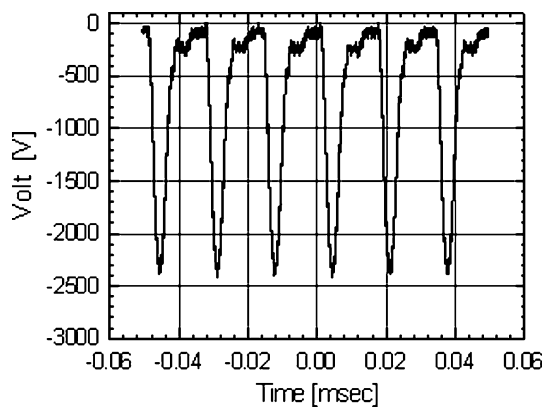
**Fig. 6** The total axial magnetic field profile for the upper and lower electro magnetic current



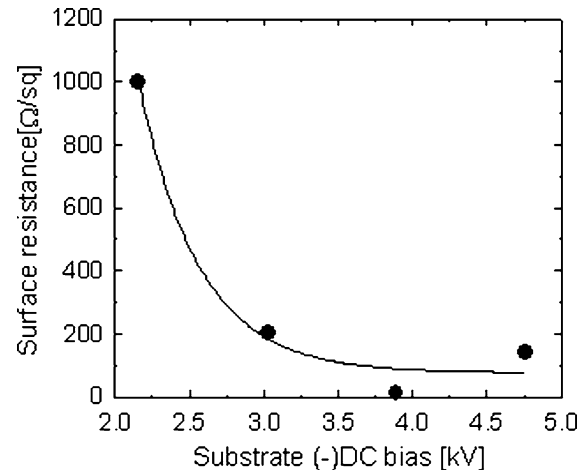
**Fig. 7** Effect of upper magnet current on deposition rate and electrical resistance of the Cu/C film. Lower magnet current was fixed as 120 A

#### Effect of periodic negative voltage from DC bias

The role of DC bias with periodic negative voltage for Cu/C film deposition is acceleration of positively charged copper ions near the substrate surface. The typical DC bias employed is shown in Fig. 8. Preparation of the metallic film was possible only at a 60 Hz frequency. Only polymeric film was deposited at a 120 Hz frequency. Therefore, it appears that supersaturated concentration of copper ion are not obtained at high frequency but can be only secured at some optimum frequency of the negative voltage from DC bias. Figure 9 shows the effect of DC bias voltage on electrical resistance of the film. With the increase of negative voltage, the electrical resistance of the film sharply decreases initially and then slowly to the  $10^8$ – $10^0$  ohm/sq ranges.



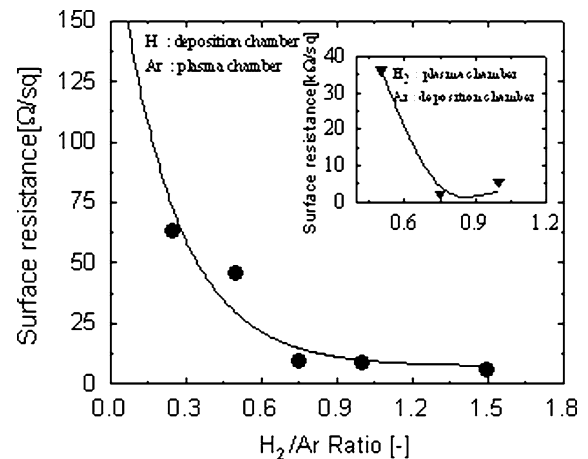
**Fig. 8** Voltages patterns from DC bias at 60 Hz



**Fig. 9** Effect of periodic negative voltages on electrical resistance of the Cu/C film

#### Effect of H<sub>2</sub>/Ar mole ratio

Figure 10 shows the electrical resistance variation of the Cu/C films deposited on PET at ambient temperature as a function of H<sub>2</sub>/Ar mole ratio. The highest resistivity is observed at 0% H<sub>2</sub> content, but it sharply decreased with an increase of the H<sub>2</sub>/Ar mole ratio. H<sub>2</sub> and Ar feeding points in the ECR-CVD chamber also affected the electrical resistivity of the film prepared. As shown in the figure, selection of different gas feeding rates with the same H<sub>2</sub>/Ar mole ratio led to different values of electrical resistivity. The reason for these results can be explained by the existence of an H<sub>2</sub> concentration gradient in the ECR-CVD reactor. An increase in H<sub>2</sub> content leads to a decrease in electrical resistivity because a homogeneous copper-rich film is



**Fig. 10** Effect of H<sub>2</sub>/Ar ratio on electrical resistance of the Cu/C film

formed under hydrogen rich conditions. On the other hand, a carbon-rich film with high electrical resistivity was prepared at a low content of hydrogen.

## Conclusions

Combination of ECR plasma with high-density ionization and a periodic negative voltage of optimum frequency makes it possible to deposit Cu/C films on the polymer substrates by MOCVD at ambient temperature. It was found through structural and chemical analyses of the Cu/C films that the ratio of Cu/C in the film depends on the process parameters such as DC bias voltage and H<sub>2</sub> content. Increase in H<sub>2</sub> content, microwave power, magnet current and the negative voltage brought on copper-rich film formation with low electrical resistance. On the other hand carbon-rich films with low electric resistance were prepared by decreasing process parameters aforementioned. Electrical resistance of the films is controlled at the 10<sup>8</sup>–10<sup>0</sup> ohm/sq range by process parameters of the ECR-MOCVD system.

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