전자사이크로트론공명플라즈마 상온화학증착에 의해 제조된 **Cu/C** 박막특성

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Characteristics of Cu/C Films on Polymer Substrate prepared by room temperature ECR-MOCVD

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Introduction

Preparing metallized polymer by metal organic chemical vapor deposition (MOCVD) is of considerable interest since it enables the production of metal film of good adhesion with polymer substrate for microelectronic packaging, organic LCD and electromagnetic interference (EMI) shielding [1,2,3]. However, most established MOCVD methods for the preparation of metallic films, especially for copper film, employ thermal or plasma CVD procedures at operating temperatures in the range of 200 to 380°C. Therefore, employment of polymer substrate for the deposition of copper thin film, which requires room temperature MOCVD, was not tried. Recently, we found that MOCVD is possible at room temperature when periodic negative voltage is applied near the polymer substrate. The periodic negative voltage induces ions and radicals to have nucleation reaction on the surface of the substrate. The high efficiency in exciting the reactants in ECR plasma coupled with periodic negative voltage allows the deposition of films at room temperature.

In the present study, the structural and chemical analyses of the Cu/C films were carried out and their electrical surface resistance was determined as a function of H_2/Ar mole ratio, microwave power, periodic negative voltage and current of magnets.

Experimental

Cu/C thin films were deposited in the ECR-MOCVD reactor. Polymer sheet with low thermal resistance such as PET (Polyethylene terephthalate) was used as the substrate. Metal organic precursor, $Cu(hfac)_2$ (1,1,1,5,5,5,-hexafluoro-2,4-pentandione) with purity 99.9% was heated at 110°C in a silicon oil bath, and argon carrier gas conveyed the evaporated precursor vapor to the substrate. Substrate temperature was maintained at room temperature. The feed rate of $Cu(hfac)_2$ was controlled by adjusting bubbler temperature and carrier gas flow rate through it. Hydrogen gas was fed to the CVD reactor to control the properties of films deposited.

In order to compare the characteristics of ECR-MOCVD with those of PVD, a magnetron sputtering system was employed to deposit Cu film. Films were deposited in a cylinder type reactor(Φ400mm×H300mm) with an rf planar magnetron facing down with the polymer substrate placed 10cm from the target. A copper target is used as the metal source and Argon is fed as carrier gas. The copper target was placed on the cathode and connected to an 13.56 MHz radio frequency generator with matching network and power source of 1kW maximum. Thin

films were prepared at rf power of 120W after maintaining argon gas flow 20sccm with a mass flow controller. A constant working pressure of 20mTorr was maintained throughout the magnetron sputtering.

Deposited films were examined with XRD (Rigaku, Geigerflex), SEM (Hitachi S-4200), XPS (PHI 5800), AFM (Park Scientific Instrument) and AES/SEM (Perkin-Elmer φ-670). Sheet resistance of films determined by four-point probe measurements(CMT-SR1000N). Adhesion properties of the prepared films were measured in accordance with modified ASTM D5179-91. The coated side of the substrate of 6mm diameter was attached on the surface of a homemade jig with a cyanoacrylate adhesive and tested with Instron®(Model 1127). Measurement was conducted at room temperature and humidity at cross-head speed of 2mm/min.

Results and discussion

The electric charged copper ions and carbon cluster, fluorine, hydrogen ions are generated by decomposition of the precursor, $Cu(hfac)_2$ in ECR plasma environment. Most of Cu ions formed in the ECR-CVD reactor are positively charged, but carbon clusters are negatively charged. If negative voltage from DC bias were not existed, only reactive hydrocarbon fragment interacts with activated PET surface and then the hydrogen enriched polymeric film should be formed. However, when DC bias are coupled with ECR plasma, the periodic negative potential field from DC bias induces positively charged copper ions. So, the positively charged copper ion concentrations are abruptly increased near the substrate. When the copper ion reached supersaturated state for film deposition, they can grow above the critical nucleus size on the surface of the polymer substrate. At the same time, plasma polymerization reaction proceeded between hydrocarbon radicals and the dangling bonds on the film. Thus, copper clusters were uniformly embedded in hydrocarbon matrix.

The chemical state of the film surface prepared ECR-CVD was analyzed by XPS. The obtained spectra of C1s, O1s, F1s, Cu2p are shown in Figure 1. The component of copper precursor, $Cu(hfac)_2$, was incorporated into the surface structure of the films. The C 1s 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 $Cu(hfac)_2$. Observing O1s and F1s spectra, oxidized copper peak (530.5 eV) and CF_n bonding (688eV) were formed. The very small CF_n peak indicated that most of fluorine functional groups from the precursor converted to volatile hydrogen fluoride by gas phase substitution reaction with reactant hydrogen. As a results of curve fitting for Cu2p spectrum, metal copper (932.7 eV) and CuO, Cu_2O (933.6 eV) , $Cu(OH)_2$ (935.2 ev) peaks are observed. The strong influence of oxygen is both from the dissociation of precursor and oxidation in atmosphere. Figure 2 shows that typical variation of Cu, C and O Auger signals versus sputtering time for the specimen from ECR-CVD and sputtering. In the specimen of Cu/C film from ECR-CVD, AES depth profile shows the formation of homogeneous Cu/C layer with average composition about 80% at Cu and 20% at C. The content of oxygen in the film was negligible. By observing the chemical shift of the Auger carbon peak at the beginning of the profiles of Figure 2, we can construe that some of carbon converted to carbide form due to chemical bonding and organic carbons network was formed in the deposited film. Figure 3 shows the effects of microwave power and magnet current on deposition rate and electric resistance of the film prepared. Those results indicated that increase in microwave power gave rise to higher degree of ionization and increase of magnet current also brings on an increase of ionization because magnetic intensity increases the electron path

and raises possibility of inelastic collision

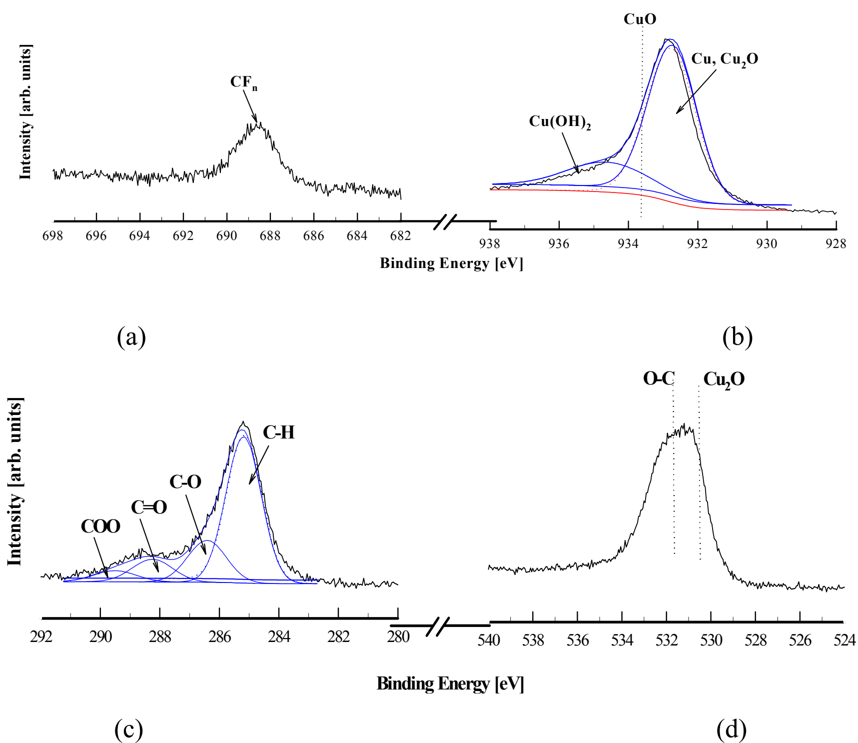

Figure 1. (a) C1s, (b) O1s, (c) F1s, (d) Cu_2p spectra of Cu/C films prepared by ECR-MOCVD.

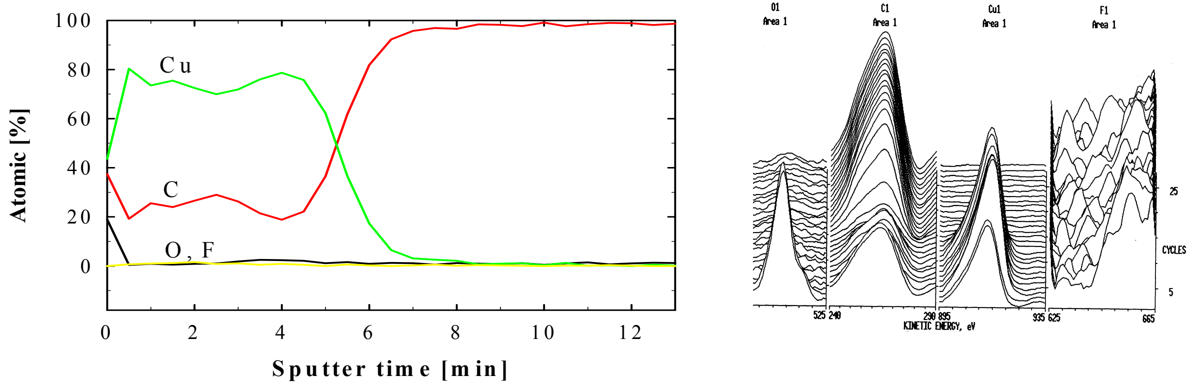

Figure 2. AES sputter depth profiles of the Cu/C layer structure prepared by ECR-MOCVD.

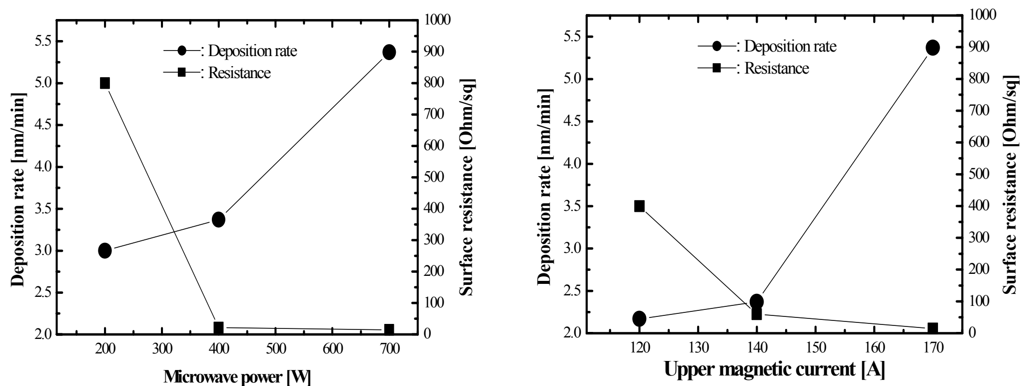

Figure 3. Effects of microwave power and upper magnet current on deposition rate and electric resistance of the Cu/C film. Low magnet current was fixed as 120amphere.

Conclusion

Chemical and physical properties of Cu/C films prepared by ECR-MOCVD are reported to give insight into the effects of microwave power and magnet current on electrical resistance of those materials. ECR plasma enhances ionization and path of electron by resonance under magnetic field. High efficiency excitation of the reactants in ECR plasma coupled with periodic negative DC bias allows the deposition of films on substrates at room temperature. It was possible to synthesize copper/carbon composite film at room temperature with good adhesion. The increase of microwave power and magnet current is believed to promote ionization, which leads to increase in roughness through higher deposition rate and higher cross-link of film surface. However, higher value of microwave power also brings on surface etching and it results in low r.m.s surface roughness. Electrical properties of the films were closely related to the process parameters such as microwave power and magnet current. The increase in H_2 flow rate, microwave power, magnet current brought on copper-rich films with low electrical resistance.

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