Preparation of Cu Films on Polymer Substrate by ECR-MOCVD coupled with DC bias at room temperature

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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 and organic LCD.

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, Cu/C thin films were deposited in the ECR-MOCVD reactor. 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^{o}C in a silicon oil bath, and argon carrier gas conveyed the evaporated precursor vapor to the substrateThe DC bias that generated a periodic negative voltage was used in order to induce positively charged ions on the surface of substrate. The employed DC bias voltage near the polymer substrate was fixed at -4kV in this work

Figure 1 shows the XRD spectrum for the samples prepared with three different levels of H_2 supply to the plasma. The sample deposited without an H_2 supply to the plasma shows no peaks, except for the semicrystalline PET. However, with increased H_2 supply to the plasma, Cu (111) peaks are clearly observed. This indicates that Cu clusters within the films are oriented in the (111) direction with the addition of H_2 gas to the plasma. This result suggests that the introduction of hydrogen enables the Cu deposition on the PET.

The surface morphology was observed by SEM and the results are shown in Fig.2. Without an H_2 supply to the plasma, it can be seen that the film consists of fine grains embedded in an amorphous matrix, as seen in Fig. 2(a). However, with the introduction of H_2 to the plasma, the films exhibit enlarged grains, as seen in Fig. 2(b). These results are consistent with the XRD results in Fig.1, which means that the larger Cu grains are formed in metal-organic composite films with the introduction of H_2 to the plasma**.** The cross-section of the films shows that the Cu/C:H film was deposited tightly on the PET without void boundaries.

Fig.3 shows the AES depth profiles of the Cu/C:H films deposited with an H_2 content of 0 % and 13 %. Near the interface, diffusion of Cu and C on the PET substrate is observed. Oxygen exists only on the surface, which is shown via the surface oxidation. Fluorine was not found within the film through fluorine was in the source compound. These results clearly show that byproduct incorporation in the film is negligible. The profile of the films deposited without the addition of H_2 gas to the plasma (Fig.3(a)) shows the formation of more carbon contents, while that deposited with H_2 gas introduction shows the formation of copper-rich films with a homogeneous composition (Fig.3(b)). Hydrogen may lead to both the formation of stable volatile.

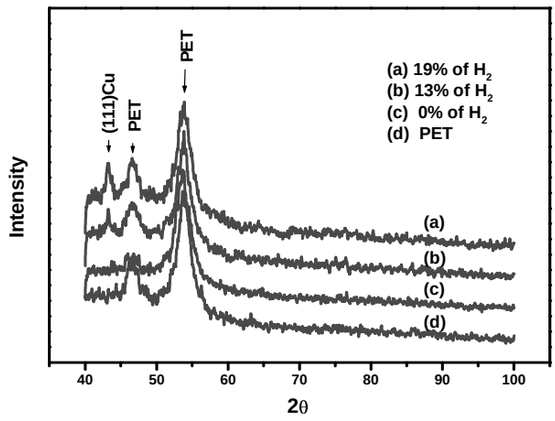
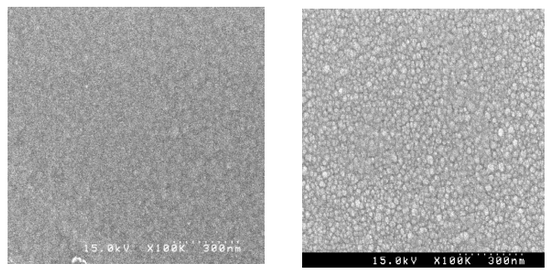


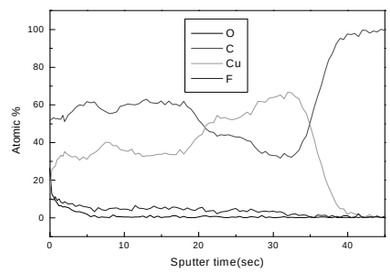
Figure 1. XRD patterns of films deposited by ECR-CVD (a) with 0% of H_2, (b) 13% of H_2 and (c) 19% of H_2 to the plasma.



(a) (b)

Figure 2. Scanning electron micrography of films prepared (a) without H_2 gas to plasma and (b) with the addition of H_2 gas to the plasma

(a)



(b)

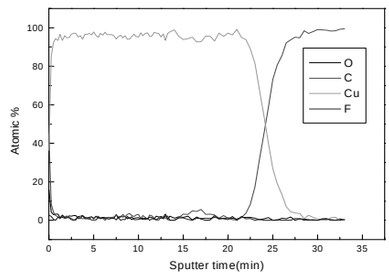


Figure 3. Auger depth profiles of films prepared (a) without H_2 gas to plasma and (b) with the addition of H_2 gas to the plasma.