Low Temperature Deposition of Cu Thin Film on Polyimide Using RF-driven Atmospheric Pressure Plasma Jet in Nitrogen Atmosphere

Peng Zhao^{1,2}, Wei Zheng³, Yuedong Meng² and Masaaki Nagatsu^{1*}

¹ Graduate School of Science and Technology, Shizuoka University, 3-5-1, Johoku, Nakaku, Hamamatsu, 432-8561 Japan

² Institute of Plasma Physics, Chinese Academy of Science, Hefei, 230031 China

³ Research and Technology Center, Yazaki Corporation, Susono, Shizuoka, 410-1194 Japan
tmnagat@ipc.shizuoka.ac.jp

For fabrication of future flexible electronic devices, Cu films on polyimide substrate were prepared by atmospheric pressure plasma (APP) jet. The plasma jet was driven by an radio frequency (RF, 13.56 MHz), and ignited by applying RF power of 300 W to the coil after plasma-gas introduction (Ar: 1000 sccm, H₂: 10 sccm). A copper water-cooling heat sink is used as a substrate platform to avoid the thermal damage of polyimide by APP jet. To prevent the oxidation of deposited film, the effects of adding H₂ into Ar plasma gas and replacing air to nitrogen atmosphere were studied. Stylus profiler was used to measure a thickness of each film. The surface morphology and roughness of the Cu films were measured by AFM and SEM. The characterization of Cu films on polyimide was investigated with XPS.

Keyword: atmospheric pressure plasma jet, polyimide, Cu film, Deposition

1. Introduction

Polyimide (PI) has good thermal stability, chemical-stability and mechanical properties such as a high modulus of elasticity. Accordingly, copper (Cu) coated PI films are commonly used as flexible printed circuit boards in the electronic industry [1-3]. To meet the growing needs for patterning of precise fine circuits in future, we developed a technique to deposit Cu thin film on polyimide by employing atmospheric pressure plasma (APP) jet driven by radiofrequency (RF) power. In this technology, however, there remain several critical issues, such as avoiding the oxidation of Cu material during the process in atmospheric air, and improving adhesion properties of Cu films on polyimide substrate [4, 5].

In our previous work, we found that adding H₂ gas significantly increased deposition rate and decreased oxidation. But Cu film oxidation could not be avoided in air. To solve this issue, we deposited Cu film in nitrogen atmosphere. The effect of nitrogen atmosphere on the characteristics of Cu films deposited on polyimide sheets was investigated. In Nitrogen atmosphere, oxidation still

exists because polyimide includes two oxygen atoms. So in the recent work, we still use hydrogen assisted Ar plasma to prevent the oxidation.

Fig. 1 Schematic sketch of the experimental setup for Cu film deposition on polyimide.

We investigate the effects of plasma characteristics to Cu deposited on PI film by $\pm$ -step stylus profiler, Field Emission Scanning Electron Microscope (FESEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS, ESCA), and four-point probe measurement.

2. Experimental

The scheme of APP jet for Cu film deposition on polyimide is shown in Fig. 1. The jet applied an induction coil which was wrapped four times around a quartz tube (3mm in outer diameter) and had water flowing through it for cooling purposes. One end of the coil is connected with a capacitor bank that is continuously tuned to match the plasma's inductance, and the other is connected with grounded electrode. The APP jet is driven by a RF (13.56 MHz) power generator between 200 and 500 watts. Cu wire source material with a diameter of 1mm was inserted into the quartz tube and was also used as a tesla coil to ignite plasma. When deposition in nitrogen was studied, the plasma jet is placed in a chamber full of nitrogen.

By ion sputtering and resistive heating of Cu wire by RF plasma discharge, Cu films are deposited on polyimide with a source-substrate distance of 1 mm. Ar (1000 sccm) or Ar/H₂ (1000 sccm/10 sccm) gas with purity 99.999% fed into the quartz tube, was applied to generate APP jet. The Cu particles derived from Cu wire were dispersed on a substrate deposition. After deposition, the Cu film was solidified by rapid quenching with alcohol solution. The previous study showed that alcohol affects on the reduction of Cu oxide in a higher temperature [6].

A copper water-cooling system is used as substrate platform, and quality of the Cu films shows strong dependence on temperature of the substrate platform. When Cu film was deposited on polyimide without water-cooling, the polyimide surface was damaged by plasma jet if the plasma gas temperature is high enough. If temperature of the substrate platform is less than 60°C, the deposition rate is low, and moreover the adhesion between Cu film and polyimide is also low. So after many tests, it was found that the better temperature of the substrate platform was from 65 to 100°C. In order to improve deposition rate and film quality, the subject needs further study in the near future.[6,

7]. The polyimide of 0.125 mm thickness made by Nilaco Corporation was used as substrates. In order to optimize the direct coating without adhesive, the PI films were rinsed in acetone prior to the deposition process [4].

In order to discuss the effect of nitrogen atmosphere, the Cu films were deposited in air atmosphere and nitrogen atmosphere separately.

The film thickness was measured with a $\pm$ -step stylus profiler (KLA Tencor Alpha-Step IQ). The surface morphologies were observed by Field Emission Scanning Electron Microscope (FESEM) (JEOL JSM-7001F). Atomic force microscope (AFM) was used to test the surface roughness. X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA-3400) was used to detect the quality and purity of Cu film. Prior to XPS analysis, the stylus profiler was used to measure the profile of a Cu film. After Ar ion etching for 540 s in XPS analysis, the Cu film profile was measured at the same position. We could get the Ar ion etching rate from these results and calculate the etching thickness. From XPS spectra, we investigated the quality of all the etching layers in Cu films deposited by Ar gas and Ar/H₂ mixture gas. Sheet resistance and resistivity were measured by four-point probe meter.

3. Results and discussion

3.1 Cu film growth

Fig. 2 Photos of deposited Cu films by (a) Ar and (b) Ar/H₂ plasma in air for 900 s.

During the deposition process, substrates were cooled and kept at 65-100°C. By this method, the Cu films were deposited successfully on the polyimide substrate without damage. The low-temperature growth could reduce the deformation and avoid curving the polyimide substrates. Fig. 2 shows the Cu film on polyimide deposited by Ar and Ar/H₂ plasma for 900 s, in which the Cu film

deposited by Ar/H₂ plasma looks much thicker than that deposited by Ar plasma, and they were all not damaged during deposition. The films deposited in nitrogen atmosphere look similar with those in air atmosphere, but later we found the chemical compositions were tested different by XPS.

The growth rate of Cu film was defined by the thickness of films divided by the total time of deposition process. Fig. 3 shows the profiles of deposited Cu film measured by a stylus profiler. The Cu film was deposited on a Si substrate by an Ar/ H₂ plasma jet in air for 900 s, since polyimide is so soft that it was difficult to measure the Cu film thickness using the stylus profiler. Fig. 3 (a) shows that the Cu film is about 2200 nm thick for 900 s deposition; thus, the deposition rate is approximately 2-3 nm/s and the deposited Cu volume is roughly $3.8 \times 10^{-5} \text{ mm}^3$. The same film with Fig. 3 (a) was etched for 540 s by XPS Ar ion sputtering, and after then the Cu film thickness was measured as about 1850 nm, as shown in Fig. 3 (b), so the XPS etching rate for Cu deposition film was estimated roughly as 0.65nm/s. The results in nitrogen atmosphere are similar with them.

Fig. 3 Profiles of deposited Cu films by Ar/H₂ plasma in air for 900 s (a) before and (b) after XPS etching for 540 s.

3.2 Cu surface structure

The surface morphology of Cu films observed by AFM is shown in Fig. 4. We observed that there are much more clusters on the Cu film deposited by Ar/H₂ plasma than that by Ar plasma, and also the surface of the PI film become rougher when H₂ was added into Ar plasma.

Fig. 5 shows the SEM images on the film surfaces after (a) Ar plasma and (b) Ar/ H₂ plasma depositions in air for 900 s, and (c) Ar and (d) Ar/H₂ plasma deposited film etched by Ar ion

Fig. 4 AFM images of Cu film surface on polyimide deposited by (a) Ar and (b) Ar/H₂ plasma.

Fig. 5 FESEM images of Cu film surfaces deposited by (a) Ar and (b) Ar/H₂ gas mixture plasmas in air for 900 s, and (c) Ar plasma and (d) Ar/H₂ plasma deposited films etched by Ar ion beam of the XPS instrument for 540 s.

etching of XPS for 540 s. In Fig. 5(a), the granular deposits having 20-200 nm in diameter were discretely formed on substrate. On the other hand, in Fig. 5(b), the whole area of the substrate was fully covered with the granular deposits in diameter of 50-200 nm together with some larger grains with 300-400 nm. The uniformity of deposits area and deposition rate of Cu film were much improved by H_2 addition. Fig. 5(c) shows a SEM image of an Ar plasma-deposited Cu film surface after ion sputtering for 540 s by the XPS system. In contrast, the Cu granular deposits on the Cu film surface deposited by the Ar/ H_2 plasma have a much higher density, as shown in Fig. 5(d). From Fig. 5 (c) and (d), we found Cu granular deposits were inserted into polyimide surface, which improved the adhesion of Cu film and polyimide. The results in nitrogen atmosphere are similar with them.

3.3 XPS analysis

To obtain the surface information on the chemical composition, the deposited Cu films were analyzed with XPS. Typical XPS spectrum in Cu 2p of the film is shown in Fig. 6. The sharp Cu peak was obviously observed when small amount of H_2 gas was introduced in Ar plasma.

In the case of H_2 gas addition, a component was clearly detected at 933.1 eV corresponding to Cu and/or Cu_2O [7-9]. Moreover, another component around 935.2 eV which assigned to CuO and/or $Cu(OH)_2$ was decreased by H_2 addition. The formation of Cu oxide is due to the oxidation reactions of Cu with O_2 , excited oxygen and water vapor in air. For understanding the effect of adding H_2 into Ar plasma and nitrogen atmosphere for oxidation during the deposition, the deposited films were etched by Ar ion beam in XPS chamber. After the etching, the surface analysis was carried out again. The spectrum of the surface deposited by Ar plasma jet in air atmosphere was markedly varied as shown in Fig. 6(a). In the case of Ar plasma, there was a peak shift in the surface of the film. The relative intensity of the component at 933.1 eV increased after the etching for 420 s, and the CuO satellite peak decreased, which meant the Cu film to be oxidized at the surface. The spectrum of Cu film obtained by Ar/ H_2 plasma in air atmosphere is shown in Fig. 6(b). In hydrogen addition case, there was no peak shift of the surface prepared by Ar and H_2 gas mixture plasma after the etching (Since the intense peak at 933.1 eV corresponding to Cu and/or Cu_2O was observed,).

Fig. 6 XPS spectrum in Cu 2p regions of the Cu films deposited by (a) Ar plasma in air atmosphere, (b) Ar/ H_2 plasma in air atmosphere and (c) Ar/ H_2 plasma in nitrogen atmosphere.

The oxidation of Cu during deposition was prevented by H₂ gas addition in plasma [7, 10-12]. The spectrum of Cu film obtained by Ar/H₂ plasma in nitrogen atmosphere was shown in Fig. 6(c). Different from Fig. 6(b), not only there was no shift in the Cu peak of the film prepared by Ar/H₂ plasma in nitrogen atmosphere after every etching, but also the Cu peak intensity for the etched surface increased with increasing etching time. So the purity of Cu film was improved in nitrogen atmosphere.

Fig. 7 shows the results of Cu film by Ar/H₂ APP jet in air surface analysis at different etching time. Since the XPS etching rate for Cu deposition film was about 0.65 nm/s, after 60 s etching (corresponds to 40 nm thickness from the Cu film surface), pure Cu was observed by XPS and oxidation was significantly decreased in H₂ gas addition case. The results in nitrogen atmosphere are similar with them.

Fig. 7 XPS in wide region of the Cu film deposited on polyimide by Ar/H₂ APP jet in air.

3.4 Electrical conductivity of Cu films

We utilized the four-point probe to measure the sheet resistance of Cu films. The surface electrical conductivity of Cu film deposited by Ar/H₂ plasma in air is 2.02×10^6 S/m, but that deposited by Ar/H₂ plasma in nitrogen is about 6.7×10^6 S/m, while the pure Cu bulk conductivity is 5.71×10^7 S/m.

According to our previous research [6, 7], the reason for lower resistivity is that the CuO form reduces after adding H₂ to Ar plasma and the impurities are decreased on the interface surface.

The impurity atoms and defects, such as crystal interface, enhance the resistivity. Replacing air with nitrogen atmosphere, we found the CuO form further reduced and electrical conductivity was improved.

3.5 Deposition rate of Cu films

As we reported in previous paper [6], the deposition rate is an important factor for future industrial application of this method. The formation of copper films in polyimide films was previously reported in the case of vacuum evaporation of copper onto a fully cured polyimide substrate at an elevated temperature and lower deposition rate[13-15].

Yang *et al.* deposited Copper films on 10 cm×10 cm polyimide substrates by RF magnetron sputter system and intermittent growth technique, and the deposition rate was about 2.11 nm/s at 500 W[13]. Noh *et al.* evaluated that the deposition rate of the Cu sputtering system was 0.33 nm/s, respectively, for both the Ni-Cr and Cu sputtering[14]. The deposition time is also varied at different temperatures to form thickness detectable Cu films. Kong *et al.* found that the growth rate increased with the increase of the deposition temperature, which ranged from 0.15 nm/s at 360°C to 0.375 nm/s at 400°C for the deposition on cyano-self-assembled monolayer (SAM)-modified SiO₂ substrate and from 0.078 nm/s to 0.25 nm/s with temperature from 360°C to 400°C for carboxyl-SAM-modified SiO₂ substrate[15]. By contrast, our Cu deposition rate is higher than those previously reported, because of the gas temperature of atmospheric-pressure plasma

4. Conclusions

In this study, we carried out developing a technology of depositing Cu film directly on polyimide, by APP jet without apparent damage. In order to avoid a damage of polyimide by APP jet, a copper water-cooling heat sink was used as substrate platform, which was controlled between 65 and 100°C. The reactions that accompany H₂ gas addition are very important for preventing oxidation of the deposited Cu film in atmospheric air. The oxidation of Cu film during deposition was apparently prevented, and the Cu deposition rate was increased as a function of adding H₂ gas to Ar

plasma and nitrogen atmosphere. After adding H₂ gas to Ar plasma, all characterizations of film were verified to be improved. Comparison between deposition in air and nitrogen atmosphere, the purity and surface electrical conductivity of Cu films were increased significantly in nitrogen atmosphere. The present results show the possibility of APP jet processing for metal film deposition on polyimide surface. The future development of metal line-writing by using a focused scanned continuous plasma jet and fine deposited conductive metal lines are expected for circuit customization.

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