Preparation and Characterization of Copper Films Deposited in Hydrogen Remote Plasma by Copper(II) Acetylacetonate

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ABSTRACT

High purity and low resistive copper films are in high demand for ultralarge scale integrated process technology. By remote plasma-enhanced chemical vapor deposition, high purity Cu films can be prepared using copper(II) acetylacetonate [Cu(acac)₂] as a source material. Depositions were carried out with three types of flow tubes in order to study the reaction steps of the film formation. It is found that Cu films could be deposited only upon reaction of atomic hydrogen (H*), but not with ultraviolet radiation. Hydrogen remote plasma method makes Cu films damage free from ion impacts and free from contaminants of carbon, oxygen, and others. The resistivities of Cu film measured are about 1.8 $\mu\Omega$ cm which is close to the intrinsic value (1.72 $\mu\Omega$ cm) of bulk copper.

With the advent of ultralarge scale integrated (ULSI) technology, demand for low resistive metals compared to Al (2.70 $\mu\Omega$ cm)¹ has increased for use as a wiring material in microelectronic devices. In this respect, copper (Cu) has attracted recent interest as it has a lower resistivity of 1.72 $\mu\Omega$. ¹ Moreover, Cu also has improved characteristics for electromigration and stress migration.

Many deposition techniques such as sputtering deposition,² chemical vapor deposition (CVD), plasma-enhanced CVD, ^{3,4} and laser CVD ^{5,6} have been applied by many researchers for the fabrication of Cu films.⁷⁻¹⁰ When the step coverage of the deposits which is very crucial in fabricating microelectronic devices is concerned, CVD technique is superior to the other different techniques. Some recent works reported the possibility of fabricating Cu films by using complex organometallic compounds such as Cu(II)hexa-fluoroacetylacetonate[Cu(hfacac)₂], ^{9,12} Cu(II)acetylaceto-nate [Cu(acac)₂], ^{4,13} copper(I)(hfacac)alkyne, ¹⁴ and cyclopentadieylcoppertriethylposphine¹⁵ by CVD method. Decomposition of simple source monomers such as $\mathrm{CuCl}_2^{\ 16}$ and $\operatorname{CuF_2}^{17}$ needs higher substrate temperature. Even though in metallorganic CVD (MOCVD), many researchers use $Cu(hfacac)_2$, F atoms may be incorporated to the film as an impurity.¹² On the other hand, $Cu(acac)_2$ has no F atoms, however, the vapor pressure of the source is lower than Cu(hfacac)₂.¹⁸ Therefore, deposition of Cu films by using Cu(acac)₂ is slightly difficult with conventional MOCVD.

The deposition process of Cu films by Cu(acac)₂ in remote hydrogen plasma was investigated in the present study. The remote plasma CVD (RPCVD) can be used to differentiate the radical reaction and UV radiation-assisted reactions in high-energy ion and electron-free environment in comparison with the conventional direct plasma CVD, because the RPCVD consists of the plasma generation region, radical transport region, and deposition region separated with space.¹⁹⁻²¹ In RPCVD, as the deposition area is free from ion and electron impact, obtained films are expected to be damage free and contained no carbon, in comparison with that obtained from direct plasma deposition and electrochemical reaction (ECR) deposition.⁴ As the RPCVD is a convenient configuration to assist the radical reaction for the film formation, the precursor formation can be expected to occur in lower pressure than that of conventional CVD. Therefore, in spite of low vapor pressure, using Cu(acac)₂ which has no F atoms is strongly intended for the high purity Cu deposition.

In this paper, the physical and electrical properties of deposited films were characterized by using Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), and resistivity measurements.

Experimental

The apparatus used for this RPCVD is schematically shown in Fig. 1, where the plasma was generated by RF power source (13.56 MHz). Hydrogen (H₂, 99.999%) was fed into the flow tube with a rate of 100 sccm. Solid Cu(acac)₂ was put in a glass tube which was placed in a heating



Plasma generator H₂ Heater Substrate Vacuum pump

Cu(acac), + He

Fig. 1. Schematic diagram of experimental setup.

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Fig. 3. FTIR spectra of Cu films deposited at different substrate temperatures.

mantle in order to control the source temperature. The temperature of the source tube was varied from 100 to 200°C. Helium (He, 99.999%) was constantly flowed through the $Cu(acac)_2$ container with a rate of 5 sccm. He and $Cu(acac)_2$ vapor mixture was introduced into the H₂ plasma downstream. The distance between substrate and [$Cu(acac)_2$ + He] mixture inlet is about 3 cm. Source flow rate was estimated by measuring evaporated source weight for a given period of time.

Depositions were carried out using three types of flow tube configurations, as shown in Fig. 1 and 2. Figure 2 shows a bent flow tube (a) and a straight flow tube (b) in which two rectangular Cu plates in cross configuration were inserted. The distance between the plasma inductive coil and the substrate holder for all of the above configuration is about 60 cm. During the deposition with the straight tube, both atomic hydrogen radicals (H*) and UV radiation reach the reaction site. When the bent tube is used, UV radiation is cut and only H* reaches the reaction site. With this bent tube, the reactivity of H^* with $Cu(acac)_2$ can be investigated. When Cu plates are inserted to the straight tube as shown in Fig. 2b, H* is completely removed because Cu has a higher recombination coefficient (recombination coefficient $\gamma = 0.1$ ²² for the H^{*}. Therefore, this configuration provides information of the reaction between UV radiation and $Cu(acac)_2$ at the reaction site.



Fig. 5. X-ray diffraction patterns of Cu films deposited at 1, 400, 2, 300, 3, 100° C, and 4, room temperature.

Depositions were carried out in various conditions with respect to the chamber pressures (0.05 to 0.2 Torr), RF powers (100 to 500 W), substrate temperatures (30 to 400°C), and source temperatures (100 to 200°C), on p-type silicon substrates. The typical pressure, RF power, substrate temperature, and source temperature used for the most of the depositions were 0.05 Torr, 500 W, 300 and 135°C, respectively. The film thickness was calculated from interference fringes obtained by interference microscope. Other film properties were obtained by FTIR, Auger electron spectroscopy (AES), XRD, and resistance measurements.

Results and Discussion

Prior to the plasma deposition, thermal CVD depositions with different substrate temperatures were examined. At about 150°C of the substrate temperature, $Cu(acac)_2$ begins to dissociate and deposits organic contaminant copper metal on the reaction chamber wall. Above 200°C, copper metal was observed to be deposited on the chamber wall. However, a film deposition was not observed either on silicon or glass substrates even if the substrate temperature was increased up to 800°C. When the plasma was generated, Cu films on the substrate could be obtained with both



Fig. 4. Auger depth profile of Cu film deposited at 300°C.





Fig. 7. Deposition rate of Cu films as a function of RF power.

straight and bent flow tube configurations. The deposition rates with the above two tubes were observed to be almost the same. However, when the hydrogen radical trap consisting of crossed Cu plates was inserted into the straight flow tube (Fig. 2b), no film could be deposited even for 10 h of deposition time. These observations indicate that UV radiation cannot activate the deposition process and only H* is responsible for the activation of reaction steps leading to the film formation process.

Figure 3 shows the FTIR spectra of deposited Cu films at different temperatures. In these measurements, the film thickness was about 300 nm for all the samples. The spectrum obtained for the room temperature deposition shows very small peaks at 1700 and 2950 cm⁻¹ which correspond to C-O and C-H stretching mode vibrations, respectively. For the films deposited at 200 and 400°C, the intensities of these peaks are reduced beyond the detection limit. These FTIR data are found to be consistent with AES data. Figure 4 shows a depth profile of film composition obtained by AES measurement except for the surface region. This is a



Fig. 8. Deposition rate of Cu films as a function of substrate temperature.



Fig. 9. Relationship between the resistivity and the substrate temperature.

sample deposited at 300°C of the substrate temperature. In the bulk of the film, C and O contamination were smaller than the detection limit of 0.5%. However, AES data show that C contamination of film deposited at 30°C is about 2% in the bulk region. The oxygen contamination is less than 1%. During the deposition process, it can be considered that the carbon-containing groups are removed by atomic hydrogen via a chemical reaction. The removal of carbon by atomic hydrogen is seen to be the most efficient at around 300°C. X-ray diffraction patterns obtained for deposited Cu films (see Fig. 5) show two major peaks at 43.43° and 50.56° , which are related to Cu(111) and Cu(200) atomic planes, respectively. This observation shows that deposited films are polycrystalline regardless of the substrate temperature. The peak intensities at the above two angles increase with the increase of substrates temperature up to 300°C. Thereafter, these intensities gradually drop with further increase of substrate temperature which can be attributed to a gradual loss of polycrystallinity.

The deposition rate for the typical experimental condition is about 5 nm/min. The dependence of the deposition rate with the source flow rate is shown in Fig. 6, the deposition rate increases with an increase of the source flow rate and saturates at a source flow rate of 100 μ mol min⁻¹. This saturation occurs because all the H^{*} are consumed by the reaction with source gases. With the further increase of Cu(acac)₂ flow rate, the back diffusion of Cu(acac)₂ makes the reaction place shift upstream. When the excess source gas was added, copper films were deposited on the glass wall of the flow tube behind the source gas inlet. This happens because, Cu(acac)₂ diffuses back to the flow tube and consumes atomic H forming a film on the glass wall which results in a lower H concentration near the substrate surface. This causes a lower growth rate of Cu on the substrate.

Figure 7 shows the deposition rate as a function of RF power. With an increase of RF power, the deposition rate increases and saturates at a value of about 300 W. Since the dissociation fraction of H_2 is increased with an increase of RF power, the H* concentration at the reaction site increases with RF power. Therefore, the results indicate that at 300 W RF power, H* are sufficient to react with nearly all source material.

The relationship between the deposition rate and the substrate temperature is shown in Fig. 8. Deposition rate is found to increase with substrate temperature up to 300°C, and thereafter, deposition rate is seen to drop with further

increase of substrate temperature. The evaluated activation energies are 0.12 eV for the temperature region of 30 to 300° C and -0.25 eV for the temperatures over 300° C. This result indicates that there may be two different mechanisms for the film deposition process for the above two different temperature regions. Below 300°C, the substrate temperature assists the film formation. Above 300°C, it seems that the precursor is less susceptible for the adsorption on the substrate surface hence deposition rate is drastically decreased. X-ray diffraction data also suggest two different features for the film characteristics, as they showed variation of crystallinity, respectively, for substrate temperatures above and below 300°C. At lower substrate temperatures, partially decomposed and surface-absorbed Cu(acac)₂ may undergo some thermally assisted reaction such as surface migration and recombination. At higher temperatures, a surface absorption and desorption reactions are seen to be dominant for film deposition process resulting in a negative activation energy.

The most important characteristic of these copper films is the low resistivity which is close to that of the intrinsic bulk copper (see Fig. 9). In these measurements, the film thickness is in the range of 100 to 150 nm. Most of the samples prepared above 100°C show a very low resistivity of 1.8 $\mu\Omega$ cm except for the sample deposited at 30°C which shows a relatively high value of 2 $\mu\Omega$ cm. These values are close to that of the intrinsic bulk resistivity of 1.72 $\mu\Omega$ cm. This is considered to be due to the high purity copper films which do not contain carbon or oxygen. However, the film deposited at $30^\circ C$ of substrate temperature shows relatively high resistivity due to the organic contaminants as shown by FTIR and AES data. It is found that the most suitable substrate temperature for the formation of films without contaminations is about 300°C.

Conclusions

Cu films were deposited using $Cu(acac)_2$ as the source material in hydrogen RPCVD. Depositions were carried out with three types of plasma flow tube configurations for the selection of reactant species out of hydrogen radicals (H*), UV radiation, and ions. It is found that H* initiates the Cu film formation process and UV radiation is less significant for this process. Cu films deposited at 300°C of the substrate temperature were found to be polycrystalline without carbon and oxygen contaminants by the measurement of XRD, FTIR, and AES. These Cu films have a resistivity of about 1.8 $\mu\Omega$ cm which is close to the intrinsic resistivity of 1.72 $\mu\Omega$ cm of bulk copper. Consequently, it is shown that

hydrogen RPCVD is a promising method for high purity and low resistivity Cu film deposition.

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