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Atomic layer deposition of copper thin film and feasibility of deposition on inner walls of waveguides

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Abstract

Copper thin films were deposited by plasma-enhanced atomic layer deposition at low temperature, using copper(I)-*N,N′*-di-*sec*-butylacetamidinate as a precursor and hydrogen as a reductive gas. The influence of temperature, plasma power, mode of plasma, and pulse time, on the deposition rate of copper thin film, the purity of the film and the step coverage were studied. The feasibility of copper film deposition on the inner wall of a carbon fibre reinforced plastic waveguide with high aspect ratio was also studied. The morphology and composition of the thin film were studied by atomic force microscopy and x-ray photoelectron spectroscopy, respectively. The square resistance of the thin film was also tested by a four-probe technique. On the basis of on-line diagnosis, a growth mechanism of copper thin film was put forward, and it was considered that surface functional group played an important role in the process of nucleation and in determining the properties of thin films. A high density of plasma and high free-radical content were helpful for the deposition of copper thin films.

Keywords: atomic layer deposition, copper, inner wall, waveguide, high aspect ratio

(Some figures may appear in colour only in the online journal)

1. Introduction

Copper thin films have been widely used in the interconnection of integrated circuit (IC) devices [1, 2], seed layers [3, 4], device encapsulation [5], etc. Physical vapor deposition (PVD) technologies such as evaporation and sputtering are the most common techniques used for the deposition of copper thin films for these applications. But for substrates of internal surfaces with a high aspect ratio, the deposition of uniform copper thin films by these methods becomes extremely difficult, or even impossible, to realize.

With the development of large-capacity communication satellites, and the size and weight of waveguides used for satellite communication getting larger and larger, to reduce the weight of the waveguide, lightweight carbon fibre reinforced plastic (CFRP) is increasingly being employed as a waveguide material, and inner wall metallization is required to improve the electromagnetic properties of a CFRP waveguide [6]. Copper was an ideal candidate material for metallization of the inner wall of a waveguide due to its good electrical properties, and thin film is a preferable way of metallization. Unfortunately, evaporation or sputtering methods cannot be applied for the deposition of copper thin film on the inner wall of a waveguide because of their weak hole-filling capability and non-uniformity [7, 8]. Chemical vapor deposition (CVD), due to its sufficient conformal coverage ability, has received considerable attention, but the relatively high process temperature of CVD makes it unsuitable for plastic waveguides; furthermore, the aspect ratio of a waveguide that CVD can deal with is quite limited.

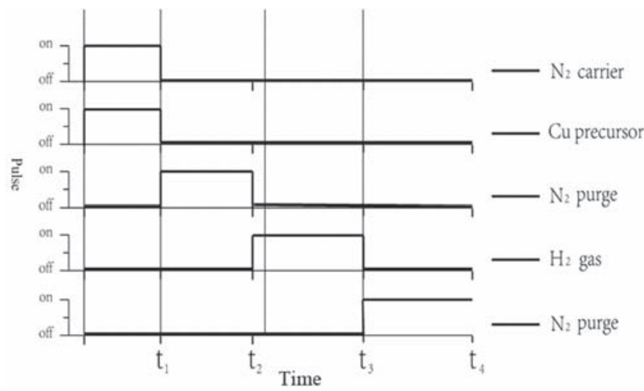

Figure 1. Pulse sequence for reactants and purge gas for copper deposition.

Atomic layer deposition (ALD) is a similar deposition method to CVD, in which an alternative pulse supply of gaseous precursors is introduced onto the substrate, and a self-limited reaction takes place to grow a single layer of thin film [9–13]. One feature of ALD is good conformality of the deposited thin film, which is independent of substrate shape, and the self-limiting growth of ALD can obtain uniformity of films over a large area [14–16].

In this paper, copper thin films were deposited on different plate substrates, as well as on the inner wall of a CFRP waveguide, by plasma-enhanced atomic layer deposition (PE-ALD), as it is well known that PE-ALD can achieve a higher deposition rate at a lower temperature than thermal ALD (T-ALD) does [17]. Surface uniformity and thickness controlling can be improved in PE-ALD as the remote plasma can produce high-density species at low pressure, and pollution from the sputtered electrode materials can be avoided, which is a major shortcoming of sputtering deposition.

2. Experimental procedure

For copper deposition by ALD, different reactants have been used by different investigators [1, 3, 18–21]. In this paper, copper(I)-*N,N′*-di-*sec*-butylacetamidinate was chosen as a precursor as it can decompose at lower temperature, and hydrogen was chosen as a reductive gas. Three kinds of substrate, namely glass plates, CFRP plates and CFRP waveguides with a rectangular cross section were selected, for the purpose of analyzing different properties and for measuring the conformality of copper thin films.

The ALD system used for the experiment was described in our previous work [22]. The home-made system consists of a stainless steel deposition chamber, a plasma system, a magnetic field coil and a pumping system. The pulse sequence of copper precursor, nitrogen and hydrogen were controlled by Labview programmable software, and the process is copper precursor/N_2 (t_1) → N_2 (t_2) → H_2 (t_3) → N_2 (t_4) → copper precursor/N_2…, as shown in figure 1. First, a copper precursor with nitrogen carrier was introduced into the reaction chamber, then nitrogen was used to purge the superfluous precursor; then a hydrogen pulse and nitrogen purge followed afterwards, in which t_1, t_2, t_3, t_4 are the pulse times for the copper precursor, purging nitrogen, hydrogen, and purging nitrogen, respectively. For comparison, both electron cyclotron resonance (ECR) and radio frequency (RF) plasma sources were used. For RF PE-ALD, two different modes were adopted, i.e., the plasma was switched on during the hydrogen pulse only, and switched on for the whole deposition process, respectively. In ECR PE-ALD, the plasma was switched on for the whole deposition process.

Table 1. Deposition parameters for ALD of copper.

Parameters	Values
Power of plasma (W)	50, 100, 150, 200, 250
Flux and time of Cu precursor (sccm/s)	20/4
Flux and time of hydrogen (sccm/s)	50/8
Flux and time of nitrogen (sccm/s)	30/2
Substrate temperature (°C)	50, 100, 150, 250, 350

For ALD, high step coverage is essential to ensure uniform film thickness, especially for a tubular substrate with high aspect ratio. The exposure required for 100% step coverage of the sidewall of the pipe, presented by Gordon *et al* [23], is:

$$t = S\sqrt{2\pi mkT}\left(4a + \frac{3}{2}a^2\right)\Big/P \quad (1)$$

where t is the time required for the precursor to reach a saturation dose, S is the saturated surface density per cycle, m is the molecular mass of the reactant, k is Boltzmann's constant, T is the temperature, a is the aspect ratio of the tube, and P is the partial pressure of the reactant near the surface.

The aspect ratio a for a tube can be calculated by the following equation [23]:

$$a = \frac{Lp}{4A} \quad (2)$$

where L is the length of the tube, p is the perimeter of the cross section, and A is the cross-sectional area.

According to the above analysis, parameters used in the deposition are listed in table 1.

In order to increase the deposition rate of copper thin film, iodoethane was introduced onto the substrate at room temperature before the copper precursor pulse. This will decompose and release iodine when the temperature rises, which can be used as a catalyst for copper deposition.

The film thickness was detected by an ellipsometer (HORIBA JOBIN YVON UVISEL, France). The square resistivity of the copper thin films was measured using a four-point probe (RTS-8, 10^{-3}–10^{6} Ω/□, China) in order to evaluate the conductive properties. An atomic force microscope (AFM) (Veeco 320, USA) was used to characterize the morphology of the films and x-ray photoelectron spectroscopy (XPS) (MK II, VG ESCALAB, England) analysis was also carried out to explore the chemical state of the thin film,

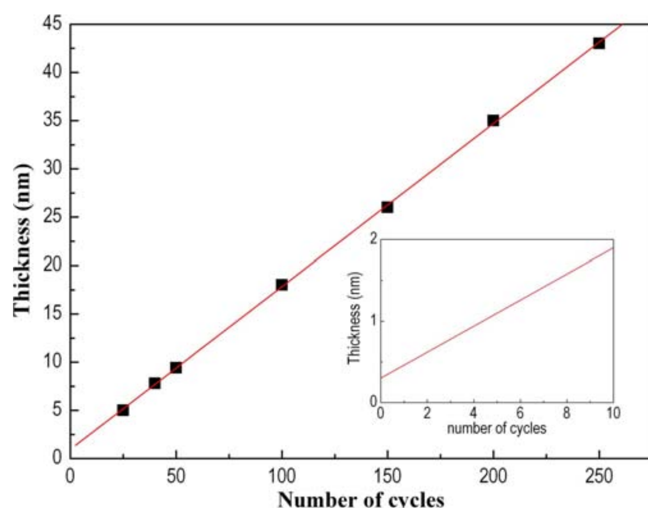

Figure 2. Relationship of Cu film thickness to the processing cycles in ECR PE-ALD. (Square dots are experimental data, and the line is a fit to the data.)

using a 50 eV pass energy and an energy step of 0.5 eV with an Al Kα (1486.6 eV) excitation source.

3. Results and discussion

When the plasma was switched on only during the hydrogen pulse for the RF PE-ALD, a thinner copper thin film was obtained with a rate of 0.013 nm/cycle; a deposition rate of ~0.1 nm/cycle was obtained when plasma was active during the whole deposition process. This indicates that the deposition rate of copper film was significantly influenced by the plasma, and surface functional group plays an important role in the process of nucleation and in determining the properties of thin films. For ECR PE-ALD, the deposition rate is 0.18 nm/cycle, which is much higher than the 0.013 nm/cycle rate of the hydrogen-only RF PE-ALD process.

As shown in figure 2, the thickness of the film increased linearly with the processing cycle for ECR PE-ALD, which means the copper film presents a self-limited growth by reductive reaction of the single layer of chemisorptive copper precursor with plasma-dissociated H atoms. On the basis of data in figure 2, the deposition rate obtained is ~0.18 nm/cycle. One possible reason for the moderately higher growth rate is that, for PE-ALD, direct interaction between the precursor and the substrate enhances film growth and limits ablation reactions. The lower deposition rate for hydrogen-only RF PE-ALD can be attributed to the low density of H atoms in the plasma-assisted stage, which reduced the density of chemisorptive copper precursor, and subsequently reduced the deposition rate.

The inset in figure 2 is a partially enlarged detail of the curve. From the inset, it can be presumed that the growth of copper thin films in ECR PE-ALD follows an island mode (which can be confirmed later by AFM characterization). The off-origin point result for the thickness-versus-growth cycles means that nucleating points grow randomly on the surface. The exact reason for this is still under investigation.

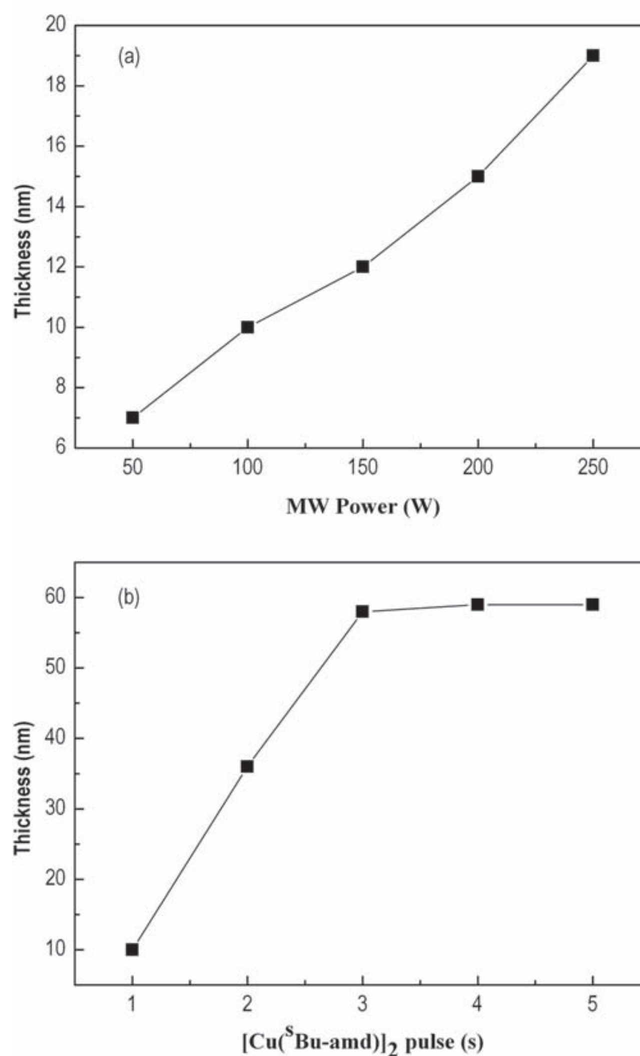

Figure 3. Cu film thickness versus (a) MW power, and (b) Cu precursor pulse time.

Influence of the power of the ECR plasma on deposition rate is shown in figure 3(a). It can be seen that the deposition rate increased with higher ECR power, and is almost linear to the power. Which means that the remote plasma led to a film growth mode different from that of the direct plasma in the RF plasma process [18, 19].

The self-limited growth mode can be confirmed from figure 3(b), with a saturated monolayer chemisorption of copper precursor even as the pulse time increased. The sequence included a copper precursor pulse for 1 to 5 s and 5 s of nitrogen purging, followed by a hydrogen pulse for 15 s, and then 5 s of nitrogen purging. From figure 3(b), it can be see that the growth rate increased as the copper precursor pulse time increased from 1 s to about 3 s, and then remained constant at ~0.18 nm/cycle with longer pulse time. The result means that even when the plasma was switched on for the whole process for ECR PE-ALD, a self-limiting chemisorption of copper precursor still occurred. For a shorter copper precursor pulse

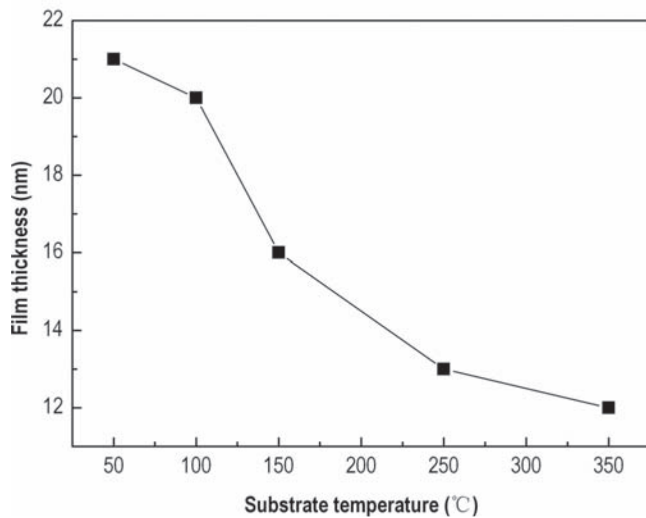

Figure 4. Influence of substrate temperature on growth rate of copper films.

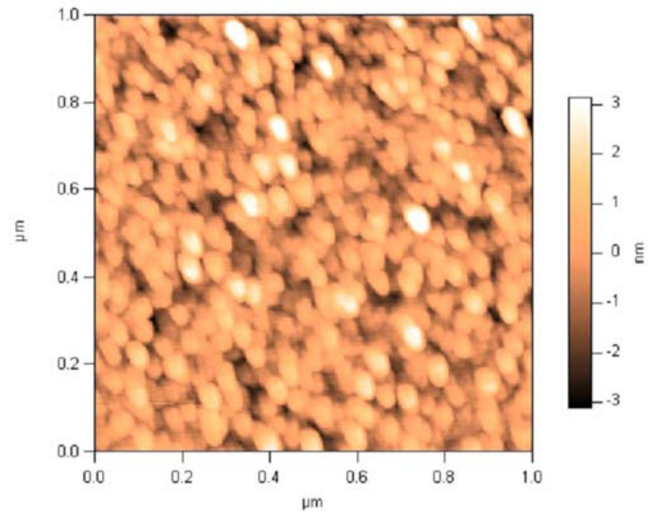

Figure 5. AFM image of copper thin film (Thickness = 13.5 nm, RMS = 0.97 nm).

time, the surface was not covered completely by chemisorptive precursor, and the coverage will increase with longer pulse time, leading to an increased deposition rate, becoming constant when pulse time is longer than 3 s.

In ECR PE-ALD, the influence of the temperature of the substrate (glass plate only) on the growth rate of copper films was shown in figure 4. Lower growth rate was obtained with higher temperature, which means that copper film growth obeys a chemisorptive mode. At higher temperature, the physisorptive precursor will be desorbed from the surface of the substrate, and a proportion of the chemisorptive precursor will also be desorbed, resulting in a lower deposition rate.

Influence of substrate temperature on the square resistivity of thin films is not quite obvious, as shown in table 2.

From the AFM image of the copper thin film in figure 5, the early nucleation stage of copper atoms can be surmised. In ECR PE-ALD, as ALD cycles increase, discrete nanoparticles in the initial phase will grow and combine, and finally form a continuous layer after about 40 cycles. The film is highly conformal and fine-grained; for a film thickness of 13.5 nm, a root-mean-square roughness of 0.97 nm was obtained.

It can also be deduced from the AFM image that, in ECR PE-ALD, when copper thin films were deposited on a glass substrate, the particles nucleated with an island mode. Due to the surface energy of the substrate, the films will present a selective growth mode. This causes the films to be discontinuous in the initial phase of deposition, and leads to a relatively high resistivity as the particles aggregate and form a film of nanoscale thickness. This should also be the reason that deposition temperature has less influence on the square resistivity of the films, as shown in table 2.

Figure 6 shows XPS depth profiles of a copper thin film sample. From the top down, the profiles are for a thin film as deposited, and sputtered by argon ions for 1, 2, 3 and 5 min, respectively. It can be seen that—apart from copper—oxygen and carbon are also included in the surface of the film, but disappear after 2 min argon sputtering. So it is believed that copper with high purity can be deposited by ALD, and oxygen and carbon are merely contaminants from the deposition chamber or from the atmospheric environment when the sample was transferred from deposition chamber to XPS, as oxygen and carbon are the most common contaminants for thin film deposition.

Table 2. Film thickness and resistivity, dependent on the substrate temperature.

Substrate temperature (°C)	ALD cycle	Film thickness (nm)	Square resistivity (R_s Ω/□)
50	100	21	94.2
100	100	20	92.7
150	100	16	95.4
250	100	13	94.6
350	100	12	93.6

Deposition of copper thin film on the inner wall of a waveguide was carried out, and then the waveguide was cut into pieces for characterization. The film thickness at different positions of a side along a lengthwise direction was detected by an ellipsometer. For a 180 mm long waveguide, after 500 cycles of ECR PE-ALD processing with substrate temperature at 100 °C, the thickness of thin films at the left end, center, and right end of the waveguide is 56 nm, 54 nm and 55 nm, respectively. The average deposition rate is 0.11 nm/cycle, with a uniformity coefficient of ~1.8% for thin film thickness. Which means that films with high conformity can be deposited for a pipe with high aspect ratio, and compared to the deposition rate of 0.18 nm/cycle for plate, the deposition rate for the inner wall is much lower.

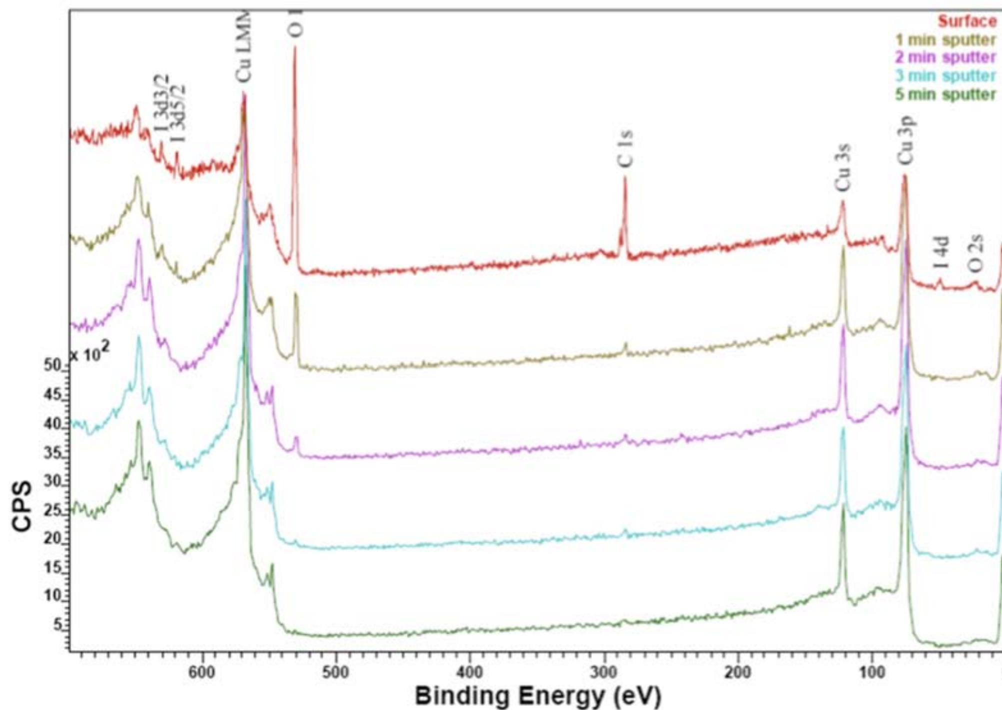

Figure 6. XPS depth profile of copper thin film.

4. Conclusions

Copper thin films were deposited by both RF PE-ALD and ECR PE-ALD. The results show that copper thin films can be deposited by both methods; the highest deposition rate of ~0.18 nm/cycle was achieved by ECR PE-ALD, which means that the plasma will affect the deposition of copper thin film, showing that high density plasma is helpful for the deposition of copper thin films. Substrate temperature does not affect the square resistivity of thin films significantly. Copper film with high purity required by waveguides can be deposited on the inner wall of waveguides by ALD, with some contaminants of oxygen and carbon only on the surface of thin films. A uniformity coefficient of ~1.8% for thin film thickness was obtained for a 180 mm long waveguide.

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