Nucleation and growth study of copper thin films on different substrates and wetting layers by metal–organic chemical vapour deposition[†]

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Abstract. Chemical vapour deposition of copper thin films on different diffusion barrier/adhesion promoter layers have been studied. Copper thin films were grown in low pressure CVD reactor, using Cu(dpm)_2 as precursor and argon as carrier gas. Growth rates, film adhesion to the substrate, and surface morphology were studied in detail.

Keywords. Chemical vapour deposition; copper thin film; surface morphology.

1. Introduction

Metal–organic chemical vapour deposition (MOCVD) has potential application in the metallization of microelectronic circuits. It gives good conformal coverage over small dimensions, even over high aspect ratio trenches, which is very difficult by any physical vapour deposition process. With rapid advances in high density integrated circuits, the interconnection metal has also become a subject of concern. Cu–Si–Al alloy, used widely for interconnection, becomes unusable because of its high resistivity ($3.4 \mu\Omega\text{-cm}$) and low resistance to electromigration. Copper, with lower resistivity ($1.7 \mu\Omega\text{-cm}$) and higher resistance to electromigration is a promising metal for interconnection (Ohmi and Tsubouchi 1992; Murarka *et al* 1993). Hence, MOCVD of copper is being studied extensively (Kaloyeros and Fury 1993). However, copper has its drawbacks: it oxidizes rapidly and diffuses easily into silicon dioxide (Schum-Diamand *et al* 1993) and silicon substrates (Weber 1988). Copper acts as a deep level dopant in silicon (Sze 1985), and if present near the interface, it gives rise to a large junction leakage current. Moreover, MOCVD-grown copper films show low adhesion to substrates (Kaloyeros and Fury 1993) making it more difficult to use in device processing technology. To overcome all these problems, a barrier layer/wetting layer has been proposed (Ding *et al* 1994). This barrier layer/wetting layer should stop Cu-diffusion to the substrate.

In view of the above requirements, we have studied the growth and surface morphology of MOCVD-grown copper films. Our effort was focused on a comparative study of nucleation, growth and surface morphology of MOCVD-grown copper films on SiO_2/Si substrate without any barrier layer/wetting layer and with a metal barrier layer/wetting layer. The diffusion barrier/adhesion promoter layers chosen were: low-melting aluminium (Al), high-melting chromium (Cr) and the refractory metal molybdenum (Mo).

We have found a slower growth rate on metal barrier layer/wetting layers compared to SiO_2/Si . The surface morphology of the films were found to be very different on different barrier layer/wetting layers. Based on our findings, chromium and aluminium seem to be effective wetting layers for MOCVD-growth of copper films on SiO_2/Si substrates.

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2. Experimental

2.1 Deposition of diffusion barrier/adhesion promoter layers

Thermally oxidized silicon wafers of $2\text{ cm} \times 2\text{ cm}$ were used as substrate. The thickness of thermal oxide was around $1\text{ }\mu\text{m}$. These wafers were cleaned in boiling trichloroethylene followed by acetone and methanol. After cleaning, the wafers were kept at 450°C in a furnace for 15 min, before loading into the deposition system.

Cr films were deposited by resistive evaporation under cold substrate conditions. Cr was evaporated from a tungsten wire basket loaded with ultra high purity chromium metal nuggets. The pressure during evaporation was 10^{-2} Torr. Because chromium sublimates and sputters, heating was done in short pulses. These pulses were controlled manually by adjusting the current. This process was found to give better films than constant heating. The films were $1100\text{ }\text{\AA}$ – $1200\text{ }\text{\AA}$ thick.

Deposition of aluminium was also performed in the same setup. A tungsten filament loaded with ultra high purity aluminium wire was used as source. Film thickness was $1200\text{ }\text{\AA}$ – $1400\text{ }\text{\AA}$.

Molybdenum films were deposited using a rf sputtering system in which the substrate was kept on a holder placed under the target. Deposition was done under cold substrate conditions. The Mo films deposited were $1000\text{ }\text{\AA}$ – $1100\text{ }\text{\AA}$ thick.

All these metal films were characterized by X-ray diffraction and resistivity measurements. Scanning electron microscopy was performed to examine surface quality of the films. All metal films were found to be very smooth having an average grain size below $0.01\text{ }\mu\text{m}$. Different parameters of these films are summarized in table 1. These metal films were stored in a vacuum desiccator and used for the study of copper film growth.

2.2 MOCVD of copper

MOCVD of copper was carried out in a vertical reactor built in our laboratory. A schematic of the reactor used is given in figure 1. This reactor consists of five main parts: (1) source or bubbler for evaporation of precursor materials, (2) gas lines with mass flow controller (MFC) and valves to enable precise control of carrier gas flow, (3) reactor chamber with IR-heated substrate holder and a graphite susceptor with an embedded thermocouple, (4) temperature controllers to enable precise temperature

Table 1. Comparison of properties of metals used as diffusion barrier/adhesion promoter layer.

Properties	Metal		
	Cr	Al	Mo
Resistivity	$13.5\text{ }\mu\Omega\text{-cm}$	$4.0\text{ }\mu\Omega\text{-cm}$	$100\text{ }\mu\Omega\text{-cm}$
Crystallinity	polycrystalline	polycrystalline	polycrystalline
Grain size	$< 0.01\text{ }\mu\text{m}$	$< 0.01\text{ }\mu\text{m}$	$< 0.01\text{ }\mu\text{m}$
Lattice	bcc($a = 2.88\text{ }\text{\AA}$)	fcc($a = 4.05\text{ }\text{\AA}$)	bcc($a = 3.15\text{ }\text{\AA}$)
Melting point	1860°C	660°C	2617°C
Layer thickness	$1400\text{ }\text{\AA}$	$1200\text{ }\text{\AA}$	$1100\text{ }\text{\AA}$

control of the substrate, bubbler and the gas lines and (5) vacuum pump with capacitance manometer and throttle valve to enable pressure control.

Copper deposition was carried out using *bis*-[dipivaloylmethanato]Cu(II) or $\text{Cu}(\text{dpm})_2$ as precursor. This precursor was synthesized in our laboratory and was found to be of high purity on elemental analysis (Goswami *et al* 1994). This metal-organic complex is a crystalline solid at room temperature, and sublimates at temperatures exceeding 80°C . Several grams of the precursor were crushed into fine powder and placed in the stainless steel bubbler. Ultra high purity argon gas was used as carrier gas for the experiments. For study of nucleation and growth, deposition was carried out for different durations using optimum deposition conditions (table 2). Different thicknesses of films were deposited on $\text{Cr}/\text{SiO}_2/\text{Si}$, $\text{Al}/\text{SiO}_2/\text{Si}$, $\text{Mo}/\text{SiO}_2/\text{Si}$ as well as uncoated SiO_2/Si wafers.

Figure 1. Schematic of the LPCVD reactor used for MOCVD deposition of copper thin films.

Table 2. Conditions for MOCVD growth of copper films.

Precursor	$\text{Cu}(\text{dpm})_2$
Bubbler temperature	120°C
Carrier gas	250°C
line temperature	
Substrate temperature	350°C
Carrier gas used	Argon
Carrier gas flow rate	50 sccm
Diluent gas flow rate	150 sccm
Pressure	10 Torr
Deposition time	15–75 min

Figure 2. Film thickness vs deposition time for MOCVD growth of copper on different diffusion barrier/adhesion promoter layers.

Figure 3. XRD pattern of MOCVD-grown copper films on different diffusion barrier/adhesion promoter layers.

2.3 Study of films grown

Gross thickness of the films deposited were measured by weight change using a semimicro balance. Resistivity of the films grown on uncoated SiO₂/Si wafers was measured by Van der Pauw method. X-ray diffraction pattern of these films were recorded on a Phillips powder X-ray diffractometer. A scotch tape peeling test was performed as a qualitative test of film adhesion to the substrate. In this test, a narrow long piece of 3M-Scotch tape was attached to the film and then the tape was pulled out. SEM micrographs of the copper films were taken using Cambridge Instruments and JEOL microscope. The electron beam energy was 20 kV and the magnification was 1 k–10 k.

3. Results

3.1 Growth

A plot of film thickness vs deposition time is given in figure 2. In general, growth is very slow at the beginning, followed by a steep increase in growth rate. On long depositions, a saturation limit is also identified. The growth rates of Cu films on different metal diffusion barrier/adhesion promoter layers were found to be lower than on bare SiO₂/Si.

3.2 Resistivity and X-ray diffraction

Resistivity of the films grown on SiO₂/Si were found to be in the range of 2.5 $\mu\Omega$ –cm to 20 $\mu\Omega$ –cm with very thin films (~ 300 Å) showing highest resistivity. We believe that the actual resistivity of the thicker films is close to the bulk value of copper (1.7 $\mu\Omega$ –cm), the higher value reported here being due to imprecise film thickness measurement and to the void structure of the films. It confirms the good quality of the deposited copper films. X-ray diffraction analysis was performed to examine the crystalline quality of the films grown. Figure 3 gives XRD pattern of copper films grown on different diffusion barrier/adhesion promoter layers. These XRD patterns show that the deposited films were of pure polycrystalline copper. No preferred orientation of copper grains was found.

3.3 Adhesion

Scotch tape peeling tests demonstrated very good adhesion of the Cu films to the SiO₂ surface. Though a few reports (Kaloyeros and Fury 1993; Ding *et al* 1994) claim poor adhesion of Cu on SiO₂/Si, films grown in our process show no blistering or delamination even at a thickness of 2000 Å. However, thicker films (> 3000 Å) on SiO₂/Si showed minor delamination with (only) the top layer peeling off with the scotch tape. Films grown on metal adhesion promoter layer suffered no damage or deformation due to peel tests.

3.4 Surface morphology

Micrographs of very thin films, showing differing nucleation density on the barrier layers, are given in figure 4. On SiO₂/Si, very high density of nucleation was found,

whereas on Mo/SiO₂/Si surface, nucleation density was very low. On Cr/SiO₂/Si and Al/SiO₂/Si, films were of thickness about 1300 Å and are in the first phase of coalescence of grains, with a very high primary nucleation density.

Figure 4. a–c.

Figure 4. SEM micrograph of thin film of Cu of specified thickness on (a) SiO₂/Si, 800 Å, (b) Cr/SiO₂/Si, 1400 Å, (c) Al/SiO₂/Si, 1300 Å and (d) Mo/SiO₂/Si, 300 Å.

Figure 5. a–b.

Figure 5. SEM micrograph of thin film of Cu of specified thickness on (a) SiO₂/Si, 3800 Å, (b) Cr/SiO₂/Si, 4400 Å, (c) Al/SiO₂/Si, 4300 Å and (d) Mo/SiO₂/Si, 2500 Å.

Figure 6. a.

Figure 6. High magnification SEM micrographs of films as in figure 5: (a) Cr/SiO₂/Si, (b) Al/SiO₂/Si and (c) Mo/SiO₂/Si. The grain shapes are to be noted.

Micrographs of thicker films show significant grain growth in the films (figure 5). On SiO₂/Si, Cr/SiO₂/Si and Al/SiO₂/Si surfaces, the grains were interconnected and closely placed, giving a nearly 100% surface coverage, whereas on Mo/SiO₂/Si, isolated large grains (10–20 μm in size) were found, giving a poor surface coverage (~40%). Another interesting feature is the structure of the grains. The films grown on metal surfaces show faceting in the grains (figure 6), whereas in films on SiO₂/Si, no such faceting was found.

4. Discussion

The general nature of the slow growth of the films at the beginning, followed by a higher rate of deposition, can be understood by invoking the concept of nucleation in a heterogeneous medium. Nucleation occurs out of supersaturation in the system. At the beginning, due to smaller size of the nuclei, the surface energy remains very high resulting in destruction of the nuclei until the size of the nuclei crosses critical value. After crossing this critical value, these nuclei grow rapidly, and then the growth rate becomes proportional to the nucleation density and adatom concentration.

The differences in nucleation and grain growth on different surfaces can be understood by introducing the concept of surface mobility of the adatom. A high adatom mobility leads to a low nucleation density and finally to isolated grain growth. Some recent simulation studies (Xu and Lu 1994) also support these observations. However, most of these simulations are of a PVD process, where the adatom is itself the depositing atom. In CVD, the two species are often different and may have very different mobilities. Hence, the effect of change of surface mobility and deposition temperature is complex in nature. However, the gross features of island growth and formation of isolated large grains (as on Mo/SiO₂/Si) can be clearly visualized using this simple concept.

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