유기금속화학증착된 구리박막의 성장과 비저항 양상

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Growth And Resistivity Behavior of Copper Film by Chemical Vapor Deposition

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Introduction

MOCVD of copper has received much attention recently for use as a metalization material in place of aluminum, because the resistivity of copper is much lower than of aluminum and it is more resistant to electromigration[1]. The motivation for the use of CVD rather than sputtering is the need to fill contact holes of high aspect ratio can be larger than 3. Copper MOCVD, however, does have its problems. The metal organics used for the source material are in liquid or solid state at room temperature and decompose when heated. Therefore the source material is usually transported to the substrate by bubbling at a low temperature, which results low growth rate.

Use of aerosol as a means of enhancing the growth rate is examined[2]. Also investigated are the differences in the growth behavior between aerosol- and bubbling- transport modes of the source material. In this paper, it is shown that the growth is transport-limited, which would have implication on the way the growth data are interpreted for the kinetics. Peculiar aspects of the growth behavior as affected by temperature and the type of carrier gas are examined and plausible explanations forwarded. Selectivity of the deposition between a barrier layer and SiO_2 is shown to prevail over a temperature range.

Experimental

Cu MOCVD is carried out in a laboratory reactor, shown schmatically in Fig. 1. The metal organic liquid source is supplied by Ultra Pure Chemicals, Inc. Once the samples are loaded onto the susceptor, the reactor is evacuated with a mechanical pump. The carrier gas passes through the bubbler and its entrained vapor is transported to the substrates. The same procedure was followed in the case of aerosol feed except for the path way of the carrier gas. The aerosol generator is not depicted in the figure but is contained in the source container.

The thickness of the grown film is measured by α-step for the growth rate, using HNO_3 solution that procedes selective etching of copper with respect to TiN and SiO_2. The resistivity is the obtained from then sheet resistance and the copper film thickness.

Results And Discussion

The Auger analysis reveal that the impurities contents are nealy undectectable, which is consistent with the results repeated in the literature for the copper deposited using Cu(hfac)VTMS. Compared with the literature results[4], the growth rate obtained in this study is not high but the resistivity is comparable or better. One limitation in our study is the maximum flow rate that can be obtained from the mass flow controller, which is only up to 500 sccm.

In the usual CVD where the source is a gaseous material, there is enough source supplied to the substrate and a question of interest is whether the film growth is dominated by surface kinetics or mass transfer. In the CVD where the source is a liquid, the first question is whether enough source material is supplied to the substrate to sustain the growth rate at given temperature and pressure.

When the source is a liquid, the maximum possible growth rate is that determined by the ideal gas law written for flow systems :

$$G_{\max} = \frac{W_c}{\rho}\frac{M_{Cu}}{2M} = 0.73Q \quad (\text{Å}/\text{min}) \tag{1}$$

where W_c is the flux of vaporized source gas, Q is the carrier gas flow rate, ρ is the copper density (8.92 g/cm^3) and M_{Cu} is the molecular (atomic) weight of copper. Note in Eq.(1) that the factor 2 is used due to the fact that two molecules of Cu(hfac)VTMS are required to form one atom of Cu on the substrate according to the mechanism of the Cu deposition[4,5].

Consider the growth behavior when the growth is transport-limited. In the region where the growth is transport limited, the growth rate should be independent of temperatrue since no surface kinetics are involved. It is noted in this regard that the growth rate is at least proportional to the temperature when the growth is limited by mass transfer. When the growth is transport-limited, then the growth rate should at least increase with incresing volumetric flow rate of the carrier gas, Q, if not porportional to Q due to a change in the bubbling efficiency accompanying a change in Q. Shown in Fig. 2 is the growth rate of copper deposited onto TiN and SiO_2 surface at 200℃, using the bubbling transport mode. It is seen that the growth rate increases with increasing flow rate of the carrier gas, although the data are somewhat scattered.

Shown in Fig. 3 is the growth rate of copper, again deposited onto both TiN and SiO_2 surface, but this time as a function of growth temperature. Argon is the carrier gas at 500 sccm. For both transport modes of bubbling and aerosol, it is seen that at least for temperatures at and above 200℃, the growth rate is practically independent of temperature although it increases somewhat in the case of SiO_2 surface. It can be concluded results that the copper growth on TiN and SiO_2 is transport-limited at least in the temperature range of 200 to 250℃.

There are two peculiar aspects of growth that can be observed in

Fig. 3 The first is that no growth takes place on SiO_2 surface up to 175 ℃. but it does on TiN surface. Therefore, selective deposition of copper only on TiN surface can be realized for temperatures lower than 175℃.

The second peculiarity has to do with a sudden increase in the growth rate at around 180℃, regardless of the transport mode and the type of substrate surface. Examine in this light the mechanism of the copper deposition reported in the literature[4,5]. Suppose for an explanation of the sudden increase in the growth rate around 180℃ up to 200℃ that the source decomposition in the gas phase and the decomposition product adsorbs. According to deposition the mechanism, the dissociation is a high activation step, requiring one adsorbed molecule to interact with a vacant neighboring site and then dissociate. On the other hand, adsorption of a gaseous species formed in the gas phase is a very low activation process. Thus, a much higher gowth rate should result when the surface reaction steps are replaced by the gas phase decomposition.

Under tranport-limited growth condition, a more efficient mode of source transport should result in a higher growth rate. This reasoning is borne out in Fig. 3. It is seen that a much higher growth is attained by the use of aerosol when compared with the bubbling mode of transport.

Concluding Remarks

The growth behavior of copper film as affected by temperature, flow rate, and the type of carrier gas has been examined. the experimental results show that the growth is limited by the amount of the source transported to the substrate, i.e., transport-limited. Therefore, a more efficient transport mode than bubbling such as aerosol should lead to a higher growth rate.

The mechanism of copper deposition with Cu(I) source has been used to explain the sudden rise in the growth rate between 175℃ and 200℃. The sudden rise has been attributed to a change in the adspecies formation : from surface dissociation of adsorbed Cu(hfac)VTMS to form the adspecies Cu(hfac) to the adspecies formation of Cu(hfac) from the precursor formed by gas-phase reaction.

References

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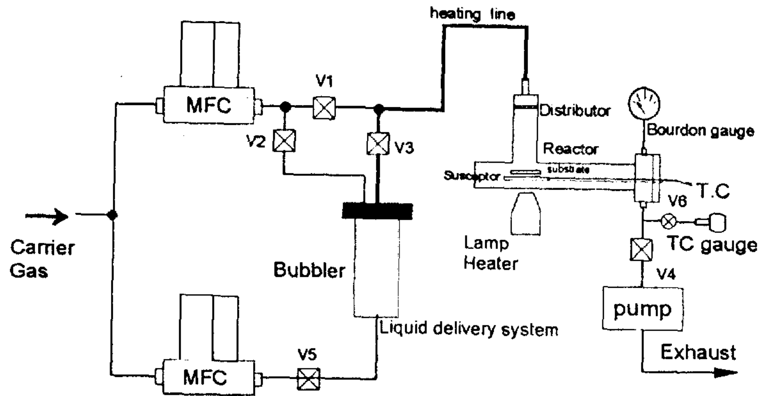

Figure 1

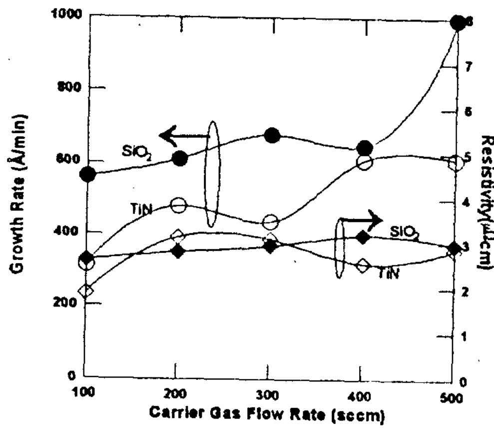

Figure 2

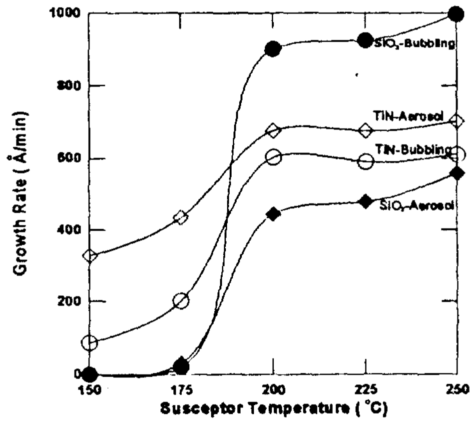

Figure 3