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Aluminum Deposition from Weekly-Excited Metalorganic Source by Hybrid-Excitation CVD

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We have proposed Hybrid-Excitation CVD to deposit aluminum from trimethylaluminum(TMA) and H_2. TMA is decomposed through plasma in a vapor phase and excited species are reacted at a substrate surface. We point out that "weak-excitation of TMA" is required to produce Al without carbon incorporation. The weak-excitation of TMA is found to be realized in radio frequency (13.56MHz) excited H_2 plasma, which is characterized by low electron density of 10^9-10^{10} cm^{-3} at 0.7 torr. We deposit Al films without carbon and oxygen incorporation. Thin Al films (about 1000Å) exhibit mirror reflection.

1. INTRODUCTION

Chemical vapor deposition of Al has been developed for fabricating VLSI interconnection because of conformal step coverage,[1)2)] ability of deposition onto a via-hole, and selective deposition on Si.[3)] Although magnetron-plasma CVD using trimethylaluminum (TMA) could produce relatively flat Al,[4)] a carbon content in the film was over several % because of immoderate decomposition of TMA and the charged particle damage might be induced. Thermal CVD Al film from tri-isobutylaluminum usually exhibited poor surface morphology.[5)] Decomposition mechanism of metalorganic(MO) source depends not only on the kind of alkyl group which is combined with metal atom but on the excited method (thermal, photochemical, or plasma excitation). It is important to control the reaction of MO source to produce Al films without carbon contamination and with good surface morphology.

We have proposed Hybrid-Excitation(HE) CVD, in which the decomposition of TMA could be controlled. TMA and H_2 as source materials were excited through plasma in a vapor phase, and the surface reaction was promoted by substrate heating and UV irradiation. Since the plasma was generated apart from wafer, the charged particle damage is not induced. We have deposited Al film without oxygen and carbon contamination in irradiated area at 250°C.[6)] Since Al had milky surface, it should be clarified what is the most important to obtain Al, and then it is necessary to improve the surface morphology.

We report that "weak-excitation" of TMA is the most important to obtain Al without carbon incorporation and that the weak-excitation of TMA can be realized in RF/H_2 discharge. Deposition of Al with mirror reflection using the HE-CVD with weakly-exciting and substrate heating is described.

2. HYBRID-EXCITATION CVD METHOD

Al films were deposited in UV irradiated area at 250°C in a previous HE-CVD.[6)] At higher substrate temperature, or at shorter distance between plasma and substrate, the effect of UV irradiation disappeared, i.e.,

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Al was deposited on the whole wafer. Substrate heating without plasma excitation could not produce Al; no film was deposited at about 250°C and an interferential AlC film was deposited at 480°C. The plasma excitation of TMA was consequently the most important to produce Al. If TMA was excessively decomposed into $Al(CH_k)_l$, C_mH_n, etc., carbon would be incorporated in deposited films. We have recognized that TMA should be decomposed into excited species such as $Al(CH_3)_2$, $Al(CH_3)$, etc. which can readily react at a substrate surface and into gaseous stable species such as CH_4, C_2H_6, etc. in order to eliminate the carbon incorporation. We call this condition

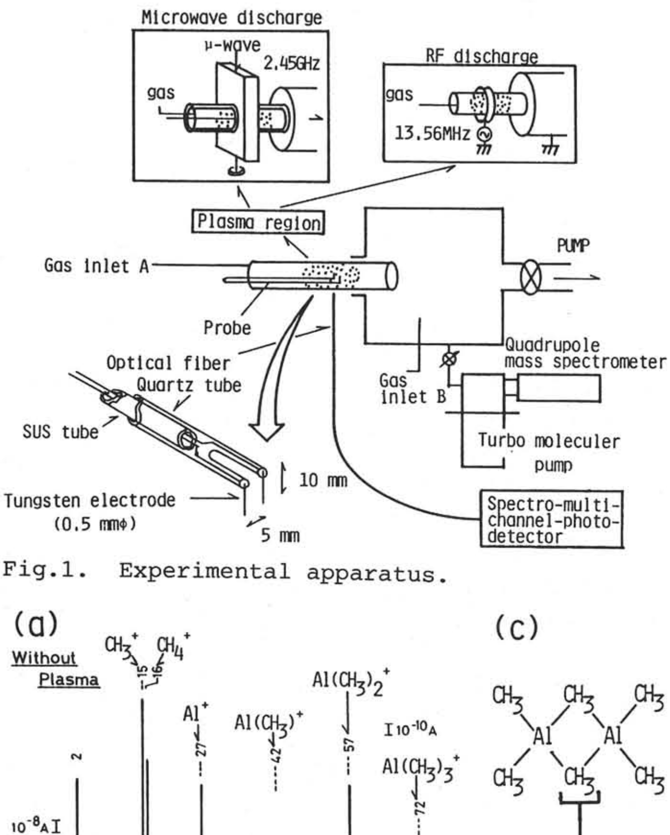

Fig.1. Experimental apparatus.

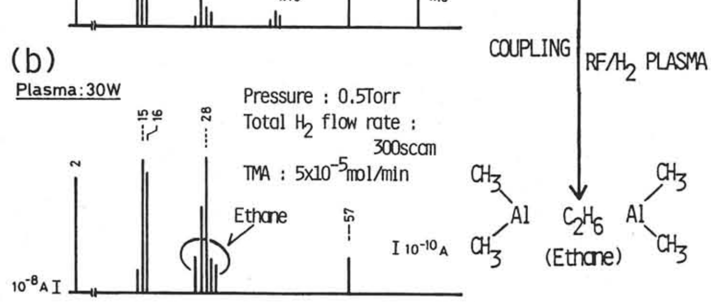

Fig.2. Typical mass spectra of TMA in H_2 with and without RF plasma. These spectra were measured in 80mmφ quartz tube.

"weak-excitation". The plasma in the usual CVD and etching process is a cold plasma, which is weakly ionized and non-equilibrium. The idea of weak excitation is different from that of weak ionization, which is characterized by a small degree of ionization. The weak excitation means that a source material is decomposed into species which can readily reacted at a substrate surface.

It is also noted that hydrogen source is required to change CH_3 group to CH_4 without abstracting H from TMA or excited TMA. H_2 is accordingly source material as well as carrier gas.

3. WEAK-EXCITATION OF TRIMETHYLALUMINUM

We evaluated decomposition of TMA in four kinds of plasma by means of mass analysis, emission spectra measurement, and probe measurement.

Figure 1 shows an experimental apparatus. TMA and carrier gas were introduced from an inlet A. RF plasma and μ-wave plasma were generated in a 35mmφ quartz tube.

Mass spectra of TMA in H_2 are shown in Fig.2. In Fig.2(b), a remarkable change was observed at 28, 29, and 30amu. From a standard fragment pattern, it was found that ethane(C_2H_6) is generated. Figure 3 shows RF power dependence of the intensity at several mass peaks. In Fig.3(a), the intensity of 28

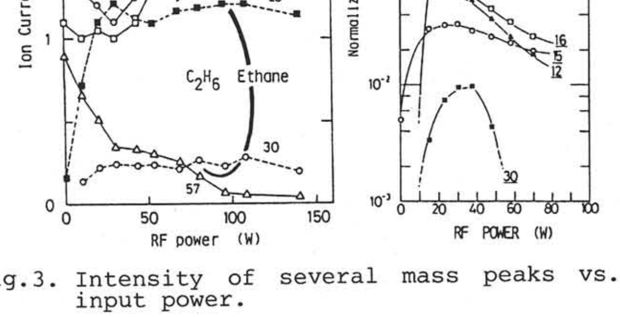

Fig.3. Intensity of several mass peaks vs. input power.

and 30amu was saturated in the range over 30W. The intensity of 15 and 16amu increased with increasing of RF power in the range over 50W. Since the ratio of $CH_3^+(15)/CH_4^+(16)$ was about 0.8, these 16 and 15 peaks were fragments of methane(CH_4). In photolysis of TMA, C_2H_6 is generated by coupling of bridge CH_3 groups.[7] In the plasma excitation, C_2H_6 may be also generated by coupling of the bridge methyl groups as shown in Fig.2(c). TMA was decomposed into $Al(CH_3)_2$ and C_2H_6 below 30W and into $Al(CH_3)$, C_2H_6, and CH_4 at higher plasma power. The weak-excitation of TMA could be, thereby, realized in RF/H_2 plasma. In RF/Ar discharge (Fig.3(b)), the ratio of $C_2H_6^+(30)/C_2H_4^+(28)$ was much smaller than 0.2. Stable C_2H_6 was not produced. The intensity

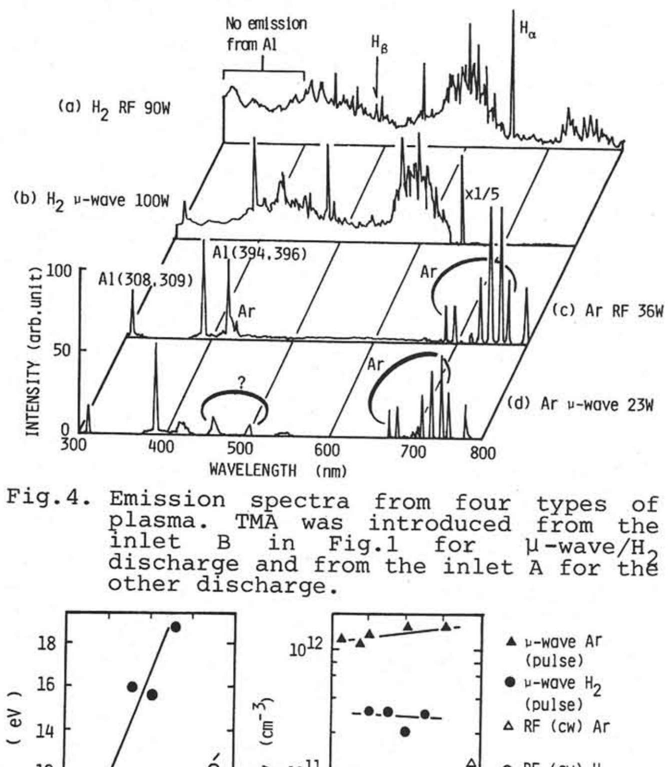

Fig.4. Emission spectra from four types of plasma. TMA was introduced from the inlet B in Fig.1 for μ-wave/H_2 discharge and from the inlet A for the other discharge.

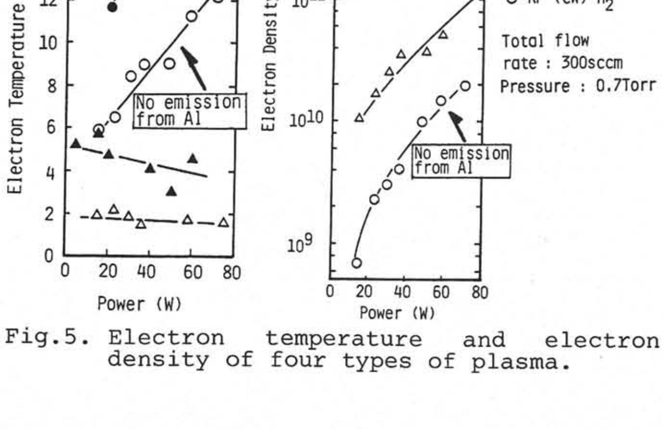

Fig.5. Electron temperature and electron density of four types of plasma.

of $H_2^+(2)$ increased and the intensity of the other peaks decreased with increasing of power. TMA was decomposed into Al, AlC compound, and unstable C_mH_n. The weak-excitation was not realized in RF/Ar plasma.

Emission spectra were shown in Fig. 4. Because TMA was decomposed into $Al(CH_3)_n$ (n=1,2) etc. and not into Al in RF/H_2 plasma, line spectra of Al were not observed accordingly. Line spectra from Al atom were observed in μ-wave/H_2, μ-wave/Ar, and RF/Ar plasma. The emission from Al atom means that TMA was decomposed into Al atom and the weak-excitation was not realized. Consequently, only RF/H_2 plasma could realize the weak-excitation among four types of plasma.

Decomposition of molecules in plasma is caused by collision with mainly electron among many kinds of particles such as electron, ion, metastable atom, etc. Electron temperature(T_e) and electron density(N_e) were measured in order to clarify what was necessary for the weak-excitation. Figure 5 shows T_e and N_e of four types of plasma. The RF/H_2 plasma, which realized the weak-excitation, was characterized by the low electron density (10^9-$10^{10}cm^{-3}$ at 0.7torr) instead of the electron temperature. Although we had expected that decomposition of TMA depended on T_e, we found that low electron density is first required to realize the weak-excitation and N_e is a more important parameter. The degree of ionization in RF/H_2 plasma was 10^{-7}-10^{-6}. This value is much smaller than that in the weakly ionized plasma of the usual CVD and etching process (about 10^{-4}). Since the weak-excitation was realized in the plasma with low electron density and TMA was decomposed into Al in the plasma with high electron density, TMA was possibly decomposed through multi-electron-collision. In order to excite TMA more precisely, the control of N_e should be required, e.g., adding a little Ar into H_2/RF plasma.

4. Al DEPOSITION WITH MIRROR SURFACE

Figure 6 shows a schematic of HE-CVD system with weakly-excited plasma and substrate heating.

Al films with about 4000Å thick showed (111)+(100) textures and the resistivity was 5-10 μΩcm. Carbon was not detected with AES and ESCA measurements, because the reaction of TMA was well-controlled to produce Al in HE-CVD as expected. Relatively high resistivity (twice of bulk resistivity, 2.6 μΩ cm) might be caused by surface roughness.

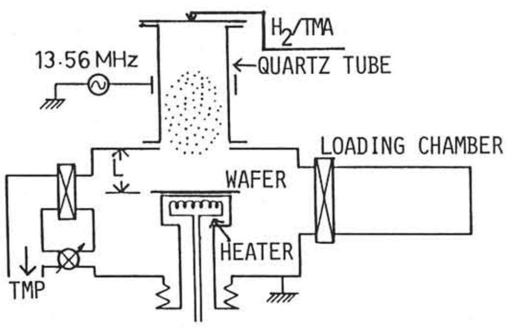

Fig.6. Schematic of Hybrid-Excitation CVD system with vapor phase excitation of RF plasma and surface reaction of substrate heating.

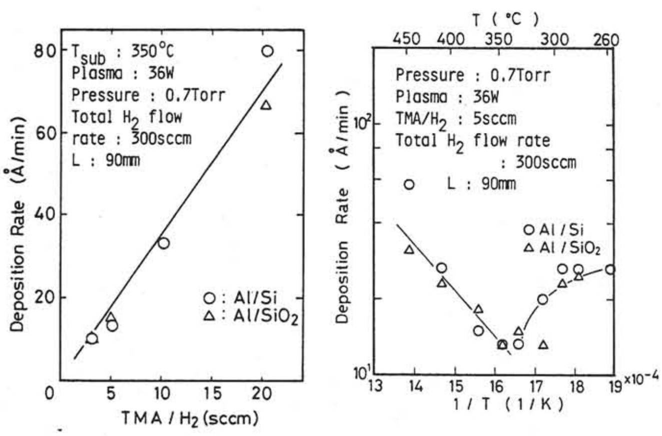

Fig.7. Deposition rate. Substrate temperature was measured with an IR thermometer (A detector was PbS.).

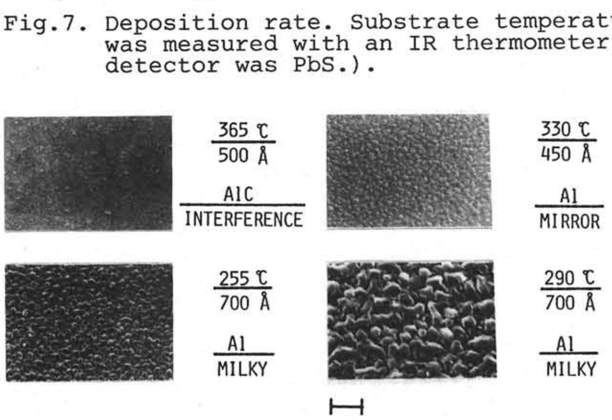

Fig.8. SEM photographs of Al surface.

We have deposited relatively thin films (about 1000Å) to optimize the growth conditions and to obtain flat films. Figure 7 shows variation of a deposition rate with a TMA flow rate and a reciprocal temperature. At TMA flow rate below 5sccm, Al films on thermal SiO_2 wafer indicated mirror reflection. At higher temperature than T_o=350°C, deposited films exhibited interferential color, which might be AlC compound. Al without carbon incorporation was deposited at lower temperature than T_o=350 °C. The films deposited near T_o have uniform grains as shown in Fig.8. Percentage reflection was 80-90% in visible wavelength region. Grain size was reduced and surface flatness was further improved with increasing of RF power near T_o. The surface morphology has been improved by using weakly-excited TMA.

5. CONCLUSION

We have pointed out for the first time that MO source should be "weakly-excited" in order to produce Al from TMA without incorporation of carbon in films. We found that the weak-excitation of TMA is realized in the RF/H_2 plasma with low electron density. Mirror-like Al films without carbon and oxygen incorporation could be deposited from weakly-excited TMA, so that the Hybrid-Excitation CVD is promising for fabricating Al film of VLSI interconnection.

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