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Effect of Operating Conditions of KrF Excimer Laser on Crystallinity of Deposits in LCVD from Mo(CO)₆

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1. INTRODUCTION

It is well-recognized in the physical vapor deposition that the structure and morphology of deposits depend on the deposition rate (D_R) and substrate temperature (T_s). These two parameters, however, are experimentally far from independent of each other in case of thermal CVD process because remarkable change of D_R can be hardly brought about without the change of T_s . The mutual independence can be expected more definitely in the case of pulsed ultraviolet (UV) laser CVD(LCVD) because this process enables the change of D_R without remarkable change of T_s and source gas-flow. From this point of view, the authors tried to investigate the effect of D_R on the structure of deposit in CVD process by changing the operating conditions of laser. Molybdenum (Mo), a promising material as interconnects for very large scale integrated circuits, was used as a target material. Few results have been given on the structure of deposits by UV LCVD though several works reported that Mo thin film containing carbon and oxygen can be deposited from Mo(CO)₆¹⁻³.

2. EXPERIMENTAL

The experimental setup for LCVD is shown schematically in Fig.1. A reaction cell with synthesized silica window was divided by two slits into three compartments. A substrate was placed in the third compartment at an angle of 60° to the incident laser beam. About 0.1 Torr of sublimated gas from solid Mo(CO)₆ placed in the glass vaporizer maintained at 300K was directly introduced into this third compartment with the flow of H₂ gas of 8.0 cm³/min(STP). The second compartment was cooled to dry ice temperature for catching the unreacted Mo(CO)₆ gas by condensing onto the cell wall. The flow of H₂ gas was introduced into the first compartment, which has an entrance window

for laser beam, for preventing remaining Mo(CO)₆ from approaching to the window. Decomposition reaction by laser was thus mainly confined in the third compartment and decomposition on the window could be avoided. No intentional heating was applied to the substrate during the LCVD process, but the third compartment was kept at 315K to warm up the gases. The total gas pressure was ca. 1.2 Torr. The sample was irradiated with unfocused laser beam from a Lumonics Model 460-SM-A Excimer Laser Equipment. A quartz plate was used as a substrate for deposits except for the deposits for composition analysis by Auger electron spectroscopy(AES), where a copper substrate was used to prevent the charge-up effect.

3. RESULTS AND DISCUSSION

Deposits with metallic luster were obtained on the irradiated spot by laser beam at various fluences (F_L) and repetition rates (R_R) of laser. The XRD pattern of the deposits showed the existence of metallic Mo and cubic Mo₂C(JCPDS No.15-457). The crystallinity of the deposits, however, intensively depended on R_R and F_L . The dependence of XRD patterns of the deposits on R_R with the $F_L=45\text{mJ/cm}^2$ is given in Fig.2. The XRD patterns due to cubic Mo₂C and metallic Mo are observable for the deposits obtained at lower R_R , while only halo-pattern are seen for that obtained at higher R_R . The dependence of the crystallinity on F_L at the fixed R_R of 10 Hz is given in Fig.3. The crystal-

Fig.1 Schematic diagram of the experimental apparatus.

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Fig. 2 XRD patterns of deposits obtained at laser fluence of 45 mJ/cm² at different repetition rates.

Fig. 3 XRD patterns of deposits obtained at repetition rate of 10 Hz at different laser fluences (F_L).

Fig. 4 Plots of peak height ratio of carbon (KLL, 272eV) to Mo(MNN, 187eV) (○) and oxygen (KLL, 503eV) to Mo(MNN, 187eV) (●) of deposit against repetition rate.

linity tends to increase with F_L . Generally, the deposit was high in crystallinity when F_L was high and R_R of pulse was low. In order to explain these results, the effects of several factors known to affect the crystallinity of the deposit were discussed.

First, temperature effect was considered since T_s generally favors to better crystallinity of the deposit. T_s measured by conventional thermocouple at $F_L=45\text{mJ/cm}^2$ were found to be 420K and 320K at 100Hz and 10Hz, respectively. As expected, T_s rose with R_R . However, the effect of R_R on crystallinity shown by Fig.2 was contrary to the speculation.

Secondly, it is also expected that a deposit will be poorly crystallized when the extent of decomposition of sample per pulse is small because of the insufficient density of nuclei over the critical nucleus size for the crystal growth. This effect can result in the production of quasi-amorphous deposits at higher R_R if the diffusion rate of Mo(CO)_6 from the ambient gas into the laser beam was too small to supply sufficient amount to react. However, D_R per pulse were found to be nearly the same for those obtained at R_R of 10 and 100 Hz (0.07 and 0.05 nm/pulse for 10 and 100 Hz, respectively).

Another factor which may affect the crystallinity of deposits is the composition of deposits. It is known that the amorphous structure of metallic materials tend to be obtained when more quantity of nonmetallic elements is included⁴ because of the increase in the covalent bonding character. The result of the elemental analysis by AES of the deposit obtained is shown in Fig.4. As seen from the figure carbon content of deposit is independent of R_R , but oxygen content decreases with increasing R_R . The understanding how the oxygen content is influenced by the experimental condition is difficult because of the background contamination from air⁵, but the results are in conflict with above assumption.

Since above three factors failed to explain the results shown in Fig.2, most probable explanation would be a slow rate of crystal growth on the surface of the substrate compared to the photolysis rate of Mo(CO)_6 at higher R_R . In the previous paper⁶, we have proposed the reaction scheme to explain the results on the rate of gas phase decomposition of Mo(CO)_6 by KrF excimer laser. The considered intermediates, formed by photolytic reaction of Mo(CO)_6 , would not be large enough to be recognized

as a crystal and re-ordering on the surface of the substrate would be required to form crystalline structure. The time required for this re-ordering seems to be of the order of time interval between successive laser pulses used in this experiment. As far as we know, this is the first observation of the effect of R_R of pulse on the crystallinity of the deposit in LCVD experiments.

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