APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 289-293 (1991)

# Wavelength dependence in photochemical vapor deposition of aluminum film using dimethylaluminum hydride

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**In photochemical vapor deposition of aluminum film on silicon using dimethylaluminum hydride, $(CH_3)_2AlH$, a surface reaction dominated below a $(CH_3)_2AlH$ pressure of 0.3 mTorr at 200 °C, which was induced only with the 160 nm band emitted from a deuterium lamp. A gas-phase reaction occurred above 0.3 mTorr at 200 °C, which could be induced by both 160 nm and 240 nm emission bands from the lamp. To distinguish between surface ad gas-phase reactions, a thickness profile was used. At 240 °C the surface reaction could be induced even by the 240 nm band, while the deposits formed under illumination of the two bands were thinner than those obtained with only the 240 nm band, indicating occurrrence of vacuum ultraviolet (VUV)-enhanced desorption. The mechanism responsible for the observed wavelength dependence is unclear. The electrical resistivity of the films deposited at 200 °C was 4.5 μΩ cm, which did not change with wavelength.**

**Keywords: Photochemical vapor deposition (CVD), aluminum film, deuterium lamp, dimethylaluminum hydride, wavelength dependence**

## INTRODUCTION

Photochemical vapor deposition (photo-CVD) enables us to deposit thin films at low temperature because photons supply at least partly the energy required for reactions leading to deposition. In addition, it is known that reaction processes involved in photo-CVD change under illumination at different wavelengths.[1] The wavelength dependence was observed for both deposition rate and film quality.

Such wavelength dependence occurs for a variety of reasons, but the most obvious case involves selective excitation of source molecules at different wavelengths. As a typical example of this type, we can cite photo-CVD of iron–nickel thin films, where the composition of photodeposited films could be changed under illumination of a nitrogen laser (337 nm) and an ArF laser (193 nm), even though an identical mixture of ferrocene and nickelocene was used.[2] A different kind of wavelength dependence was observed for growth rates of ZnSe films, where carriers generated at the growing surface promoted a surface reaction; in this case, photons should carry energy greater than the band gap.[3,4]

In a recent experiment on the photodeposition of aluminum thin films on a silicon wafer using a deuterium lamp, we found that deposits were not formed unless the vacuum ultraviolet (VUV) was included in the illumination.[5] The source gas was dimethylaluminum hydride, $(CH_3)_2AlH$, which absorbs the UV below 275 nm.[6] Indeed, the UV above 200 nm was capable of inducing growth if the wafer had been exposed to VUV beforehand. Since the previous work was concerned mostly with photodeposition of high-quality aluminum films at low temperature, the wavelength dependence then observed was not pursued further.

The objective of the present work is to study further the wavelength dependence of photodeposition of aluminum using $(CH_3)_2AlH$. Since only surface reaction was involved owing to the experimental conditions used in the previous experiment,[5] we expanded the scope to include a gas-phase reaction in the present experiment. The dependence of these two reactions on wavelength and substrate temperatue was studied in detail. However, the mechanism of the observed effects was left unresolved.

## EXPERIMENTAL

Figure 1 shows the experimental arrangement used in the present work. The stainless steel reaction cell is the same as was used in the

0268-2605/91/040289-05$05.00

*Received 1 March 1991*
*Revised 13 April 1991*

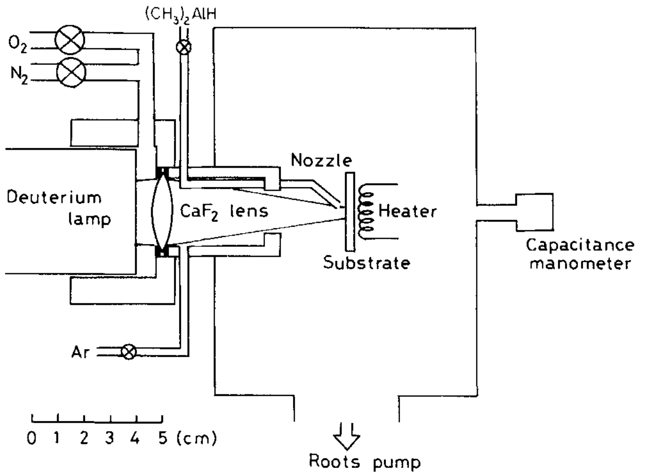

**Figure 1** Experimental arrangement used for the photodeposition of aluminum film. The scale shown at the lower left corner does not apply to the manometer.

previous work.[5] A focused beam from a 150 W deuterium lamp was used to examine the area selectivity of deposition; according to the previous work, if a deposit is formed only within an illuminated region, a surface photochemical reaction occurs for adsorbed DMAH, while a gas-phase reaction causes the loss of such localized deposition.[5]

Figure 2(a) shows the emission spectrum of the deuterium lamp obtained from the manufacturer (Hamamatsu Photonics) but modified for attenuation of the VUV below abut 130 nm by the $CaF_2$ lens. In this case nitrogen under 1 atm pressure fills the space between the lens and the lamp window. The power density for the VUV band centered around 160 nm was abut 140 mW $cm^{-2}$ on the wafer. This VUV band was eliminated by replacing nitrogen with oxygen, as shown in Fig. 2(b). On the other hand, with the help of a VUV band filter (Acton Research 160-N-1D), only the VUV band was selected, as shown in Fig. 2(c). However, the VUV was attenuated to a fraction (17%) of the original value, which made this arrangement useless on many occasions where it was necessary for comparison to keep the intensity at the same level as had been obtained without the filter.

The source gas was introduced through a $\frac{1}{8}$-inch (~3 mm) copper tube, located abut 3 mm away from the wafer. Therefore, the real $(CH_3)_2AlH$ pressure was higher than measured by a capacitance manometer. Argon introduced to protect the inner surface of the lens raised the total pressure by 40 mTorr.

The wafer and its treatment by etching were described in the previous paper.[5] Film thickness was measured by a standard stylus profilometer.

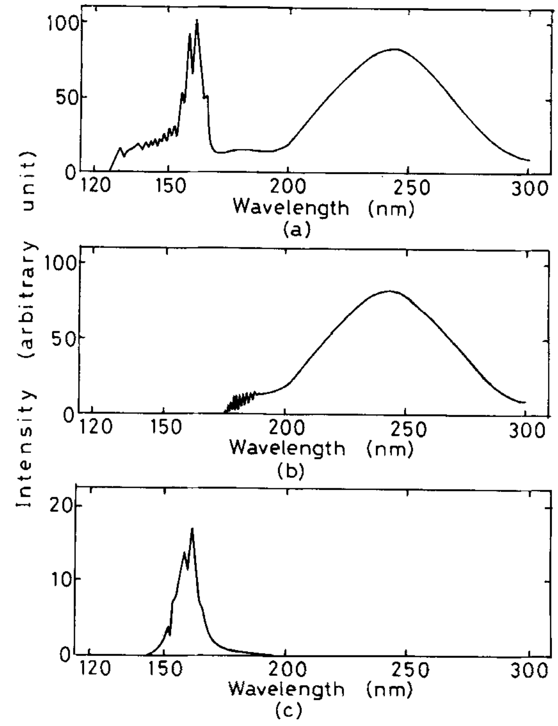

**Figure 2** Emission spectra from the deuterium lamp, as modified: (a) after passing through $CaF_2$ lens, (b) when oxygen fills the space between lamp and lens, and (c) after passing through a VUV band-pass filter. The intensity is normalized against the peak near 160 nm in (a).

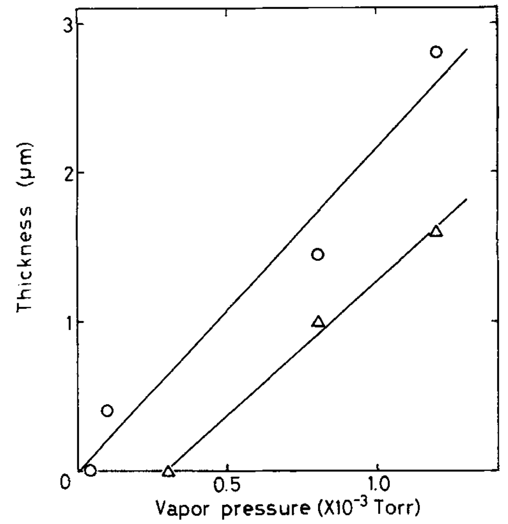

**Figure 3** Film thickness obtained at 200 °C after illumination for 10 min and plotted against $(CH_3)_2AlH$ pressure. Ring (○) and triangle (△) represent data obtained with the spectra shown in Fig. 2 (a) and (b), respectively.

## RESULTS AND DISCUSSION

Since a focused beam was used in this experiment, the photodeposited films were not uniform in thickness, and hereafter the film thickness is defined as the height measured at the center of the beam. Furthermore, films did not grow in proportion to illumination time, requiring a few minutes for nucleation. Therefore, the deposition rate was expressed as the film thickness observed after 10-minute illumination.

The deposition rate thus defined depended on $(CH_3)_2AlH$ partial pressure at a substrate temperature of 200 °C, as shown in Fig. 3. Under illumination with both the 160 nm and 240 nm bands, thickness increased linearly with $(CH_3)_2AlH$ pressure. Without the VUV band, deposition occurred only above 0.3 mTorr within the 10 minute illumination time. At $(CH_3)_2AlH$ pressures below 0.3 mTorr, VUV was required for photodeposition.

Deposition occurred selectively in the illuminated region at 0.1 mTorr and 200 °C, as shown in Fig. 4(a). A solid line was drawn to connect measured heights smoothly. From the observed profile we conclude that a photoinduced surface reaction dominates in this case. Contrary to this, at a higher $(CH_3)_2AlH$ pressure of 1.2 mTorr the deposit was almost uniform in thickness throughout the 12 mm-long substrate, as shown in Fig. 4(b). This profile was obtained under illumination with the 240 nm band. Under this condition the reaction takes place predominantly in the gas phase. The deposit was thicker at the left end of the substrate than at the right, which probably occurred because of nonuniform $(CH_3)_2AlH$ pressure on the wafer.

A mixed result was obtained at 1.2 mTorr when both 160 nm and 240 nm bands were included, as shown in Fig. 4(c). This indicates that both surface and gas-phase reactions take place. A similar profile was observed at 0.8 mTorr.

Even though the intensity was much weaker, we deposited a film at 1.2 mTorr using the VUV filter to select only the 160 nm band and obtained a mixed profile similar to Fig. 4(c) at 200 °C. Therefore, VUV can induce a gas-phase reaction, as well as the surface reaction, if the $(CH_3)_2AlH$ pressure is high.

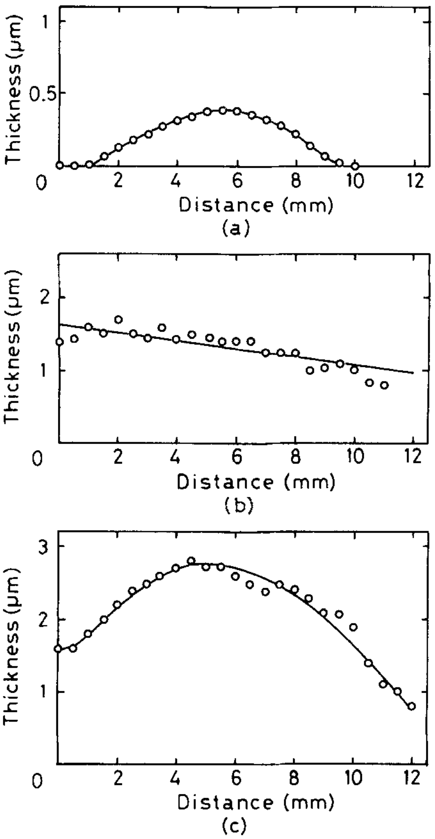

**Figure 4** Thickness profile observed at 200 °C. $(CH_3)_2AlH$ pressure and spectrum were (a) 0.1 mTorr and Fig. 2(a), (b) 1.2 mTorr and Fig. 2(b), and (c) 1.2 mTorr and Fig. 2(a).

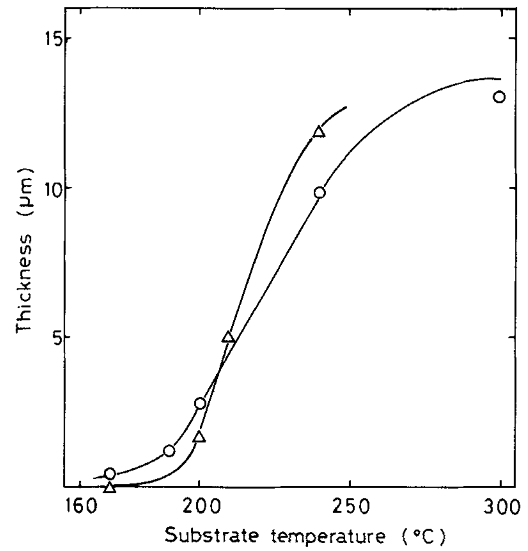

**Figure 5** Temperature dependence of film thickness obtained after 10-min illumination with spectrum of Fig. 2(a) (○) and Fig. 2(b) (△).

While all the results mentioned above were obtained at 200 °C, we found that at higher temperatures the films photodeposited under the full spectrum were thinner than those deposited under the 240 nm band only, as shown in Fig. 5. This happened even if the total number of photons involved in deposition increased, thus promoting photodissociation. Therefore, VUV photons induce some negative effect on deposition. We do not understand the mechanism for this effect, but we speculate that a photoinduced desorption may be involved. If that is the case, we are seeing a wavelength-dependent desorption.

Figure 6 shows the thickness profile observed at 240 °C under illumination with the 240 nm band and two bands together. Even without VUV, area selectivity was partly restored, which indicates that a surface photochemical reaction can be induced by the 240 nm band at 240 °C. Note that the peak in profile changes because the silicon wafer is not placed at exactly the same position.

The electrical resistivity of films photodeposited at 200 °C and 1.2 mTorr was 4.5 $\mu\Omega$ cm regardless of illumination with either the 240 nm or the full spectrum.

The mechanism for the observed wavelength-dependent deposition via surface raction is not clear at this moment. As discussed previously,[5] VUV is required only for nucleation in photodeposition at 200 °C, whilst films can grow without it once nuclei are formed. It can be assumed that $(CH_3)_2AlH$ forms a chemisorbed adlayer on the silicon wafer covered with residual native oxide, as shown for tri-isobutylaluminum, $(iB_4)_3Al$, by an X-ray photoelectron spectroscopic (XPS) study.[7] On silicon such a $(CH_3)_2AlH$ layer may absorb only VUV because of a possible shift of absorption spectra. A different kind of layer may develop on aluminum, thus making the 240 nm band effective for subsequent growth of films. An XPS study is under way to clarify the detail of surface reactions.

## CONCLUSION

For photodeposition of aluminum film at 200 °C a surface reaction dominated over a gas-phase reaction below 0.3 mTorr, whilst at higher $(CH_3)_2AlH$ pressures both reactions coexisted. Under this latter circumstance only the 160 nm band from the deuterium lamp was effective for initiation of deposition, thus revealing a wavelength-dependent nucleation process. At 240 °C the surface reaction can be induced even by the 240 nm band. A gas-phase reaction can be induced above 0.3 mTorr by either 160 nm or the 240 nm band at

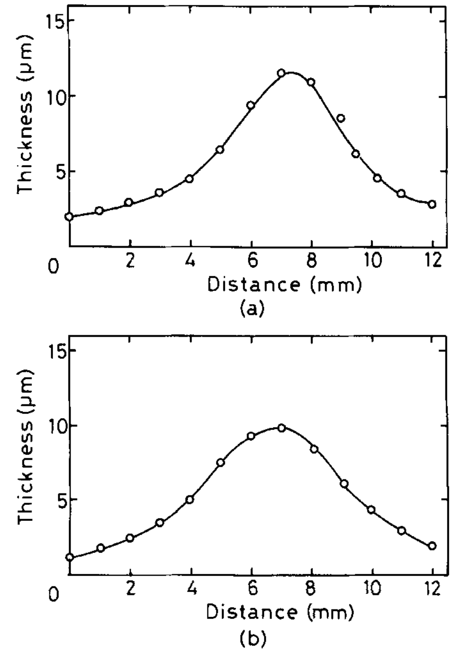

**Figure 6** Thickness profile observed at 240 °C (a) with the spectrum shown in Fig. 2(b) and (b) with Fig. 2(a).

200 °C. The mechanism responsible for the observed wavelength dependences remains unclear. At 240 °C films photodeposited with the full spectrum were thinner than those obtained with the 240 nm band only, where wavelength-dependent photoinduced desorption may be involved. The electrical resistivity was low, but did not exhibit any wavelength dependence.

*Acknowledgements* This work was carried with the Grant-in-Aid on Priority-Area Research on 'Photo-excited process' supported by the Ministry of Education, Science and Culture, Japan. We also thank the Toso-Akzo Corporation for supplying $(CH_3)_2AlH$.

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