



## UV irradiation effects in AI chemical vapor deposition on titanium nitride

Toshinari Nitta and Mitsugu Hanabusa

Citation: Applied Physics Letters **69**, 340 (1996); doi: 10.1063/1.118053 View online: http://dx.doi.org/10.1063/1.118053 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/69/3?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Sticking coefficient and growth rate during Al chemical vapor deposition Appl. Phys. Lett. **69**, 4191 (1996); 10.1063/1.116982

Early stages of diamond growth by chemicalvapor deposition monitored both by electron spectroscopies and microstructural probes J. Appl. Phys. **80**, 1830 (1996); 10.1063/1.362995

Microstructure and deposition rate of aluminum thin films from chemical vapor deposition with dimethylethylamine alane Appl. Phys. Lett. **68**, 3567 (1996); 10.1063/1.116639

Texture formation in titanium nitride films prepared by chemical vapor deposition J. Appl. Phys. **79**, 8047 (1996); 10.1063/1.362358

Enhancement of titanium nitride barrier metal properties by nitrogen radical assisted metalorganic chemical vapor deposition Appl. Phys. Lett. **68**, 2580 (1996); 10.1063/1.116190



## UV irradiation effects in AI chemical vapor deposition on titanium nitride

Toshinari Nitta and Mitsugu Hanabusa<sup>a)</sup>

Department of Electrical and Electronic Engineering, Toyohashi University of Technology, Tenpaku, Toyohashi 441, Japan

(Received 20 February 1996; accepted for publication 15 May 1996)

UV irradiation effects on Al chemical vapor deposition on titanium nitride (TiN) was investigated by using dimethylaluminum hydride at 150 °C. Al films grew thermally at a rate of 6.3 nm/min, while the UV light generated by a deuterium lamp reduced the rate to 5.2 nm/min. When TiN surfaces were oxidized, Al films started to grow only under UV irradiation. Using x-ray photoelectron spectroscopy (XPS), we showed that the adsorbates formed on the oxidized surfaces could be dissociated only when the UV light was irradiated. The XPS results also suggested involvement of photoinduced desorption in reducing the growth rate. © *1996 American Institute of Physics.* [S0003-6951(96)00829-7]

Currently, Al chemical vapor deposition (CVD) is under active investigation as a technique for fabrication of various metallization structures of advanced microelectronics devices. As the source gas, dimethylaluminum hydride (DMAH) is often used.<sup>1</sup> It can produce carbon-free Al films above 230 °C. The temperature required for the Al deposition can be lowered below 230 °C by coating the substrate with catalytic materials.<sup>2–5</sup> As an alternative, we have used photochemical vapor deposition (photo-CVD).<sup>6</sup> The UV light generated by a deuterium lamp or an ArF laser helped to lower the substrate temperature required for Al CVD to about 100 °C.

In the present work we investigated experimentally Al photo-CVD on titanium nitride (TiN). TiN serves as a barrier material that reduces interfacial mixture of Si with Al, and active investigations are under way to develop techniques to deposit Al films on TiN.<sup>7</sup> Al CVD on TiN had been investigated by other groups,<sup>4,7</sup> but the effects induced by UV irradiation remained unknown. We showed in this letter that DMAH was dissociated thermally at 150 °C owing to catalytic activity of TiN, while irradiation of the UV light generated by a deuterium lamp reduced Al growth rates. On the other hand, after exposing TiN to oxygen, Al films started to grow only when the UV light was present.

The experiment was carried out at a low DMAH pressure in order to emphasize a surface reaction.<sup>8</sup> According to x-ray photoelectron spectroscopy (XPS), the adsorbate that plays a key role in the surface reaction was not identical on the surfaces of TiN and its oxidized layer (TiON). Then, subsequent dissociation of the adsorbates differed on the two surfaces. XPS spectra showed thermal dissociation at 150 °C on TiN, while the adsorbates on TiON could not be dissociated unless the UV light was present. The XPS study also showed that photoinduced desorption of adsorbates on TiN competed with the dissociation at the initial deposition stage. We explained the observed UV-induced suppression of Al growth rates on growing Al layers by the photoinduced desorption as well. Thus, XPS studies helped us to explain the evolution of film thickness observed by a profilometer.

TiN layers, about 15 nm thick, were deposited on

Si(100) substrates by reactive evaporation in a stainless-steel chamber filled with nitrogen (99.995%) at a pressure of 5  $\times 10^{-4}$  Torr. We used a tungsten melting pot to evaporate 99.5% pure Ti metal at 1500 °C for 80 s. The electrical resistivity of TiN layers was 100  $\mu\Omega$  cm. TiON layers were formed by exposing the TiN films to 1 atm pure oxygen (99.995%) for 1 h at room temperature in the evaporation chamber. The Ti 2*p*3/2 XPS peak was observed at binding energy of 455 eV in agreement with literature.<sup>9</sup> The peak shifted to 458 eV, after exposing to oxygen.

Al films were deposited in a CVD chamber that was separated by a gate valve from the evaporation chamber described above. The chamber, 270 mm long and 152 mm in diameter, was evacuated to a base pressure of  $6 \times 10^{-8}$  Torr by a turbomolecular pump. Throughout the present experiment the substrate temperature was maintained at 150 °C by an electric heater. DMAH (2 Torr at room temperature) was blown toward the center of the substrate through a 1/8 in. stainless-steel tube without any carrier gas. We set the DMAH pressure at  $4.5 \times 10^{-5}$  Torr, which was low enough to warrant the surface reaction.<sup>8</sup>

As in our previous works, the UV light, generated by a 150 W deuterium lamp (Hamamatsu L1853) with two broad emission bands near 160 and 240 nm, was introduced into the CVD chamber through a CaF 2 lens. We focused the UV light to a spot size of about 5 mm in diameter on the substrate to increase the power density at the center of the focused light to about 140 mW/cm<sup>2</sup> for the 160 nm band. Hydrogen gas was blown against the CaF<sub>2</sub> lens, which served as an optical window, in an attempt to reduce contamination of the lens surface. Then, the total pressure in the CVD chamber increased to about  $1.5 \times 10^{-2}$  Torr during the Al deposition. We used an XPS instrument (VSW Scientific Instruments) equipped with an Al  $K\alpha$  characteristic x-ray source (1486.6 eV) in another vacuum chamber connected to the CVD chamber and evacuated to  $10^{-9}$  Torr. With the slit of an electron energy analyzer set to 4 mm×10 mm, energy resolution was about 1.3 eV, full width at half-maximum. The takeoff angle for photoelectron was adjusted to  $30^{\circ}$ .

First, we show in Fig. 1 how Al films grew in thickness on TiN layers. The film thickness was measured by a conventional stylus-type profilometer. The Al growth was compared at the center of the irradiated area and outside the

<sup>&</sup>lt;sup>a)</sup>Electronic mail: hanabusa@eee.tut.ac.jp



FIG. 1. Evolution of Al film thickness observed in (a) the irradiated area and (b) the nonirradiated area on TiN layers at  $150 \,^{\circ}$ C.

irradiated area on the same substrate. In both cases the Al films started to grow right after the introduction of DMAH. The growth rate, measured by the slope of the straight line in Fig. 1, was 6.3 nm/min for CVD, which was reduced to 5.2 nm/min for photo-CVD.

On the contrary, Al grew on TiON layers only with the help of UV irradiation, as shown in Fig. 2. The Al films became detectable with the profilometer only after 6 min. Similar evolution of Al film thickness was observed in Al photo-CVD on Si,<sup>10</sup> SiO<sub>2</sub>,<sup>11,12</sup> TiO<sub>2</sub>,<sup>13</sup> and Pd.<sup>14</sup> During this initial period, Al islands started to appear on substrate surfaces and grew in size, according to a scanning tunneling microscope study.<sup>13</sup> On TiON the Al islands were formed only when the UV light was irradiated, thus initiating the Al film growth. The Al films deposited on both TiN and TiON were highly conductive with the electrical resistivity of about 6  $\mu\Omega$  cm.

XPS Al 2*p* spectra observed at the initial stage of the Al deposition of TiN without UV irradiation are shown in Fig. 3. At 20 s the Al 2*p* peak was observed with binding energy of 74.1 eV. The spectrum changed to a broad peak at 90 s,



FIG. 2. Evolution of Al film thickness observed in (a) the irradiated area and (b) the nonirradiated area on TiON layers at  $150 \,^{\circ}$ C.



FIG. 3. XPS spectra showing Al 2p peaks observed on TiN layers without UV irradiation at 20, 90, and 480 s. The broad signal observed at 90 s was decomposed into two peaks (dotted curves), as explained in the text. The metallic Al position is marked at 72.9 eV. The magnification factor is also shown.

while a single, strong peak was observed at 72.9 eV at 480 s, which coincided exactly with the signal observed from metallic Al films.<sup>15</sup> We assigned the 74.1 eV peak to Al contained in adsorbates formed on TiN. We subtracted the 72.9 eV peak (after adjusting the peak height properly) from the broad peak observed at 90 s, and obtained a second peak at 74.1 eV. Thus, at 20 s the undissociated adsorbates existed together with metallic Al on TiN.

Next, the Al 2p XPS spectra observed under UV irradiation were taken for comparison. As shown in Fig. 4, we observed the 74.1 eV peak at 20 s again. On the other hand,



FIG. 4. XPS spectra showing Al 2p peaks observed on TiN layers under UV irradiation at 20, 90, and 480 s.

Appl. Phys. Lett., Vol. 69, No. 3, 15 July 1996

T. Nitta and M. Hanabusa 341



FIG. 5. XPS spectra showing Al 2p observed under UV irradiation on TiON layers at (a) 5 min, (b) 10 min, and (c) 20 min. The spectrum observed without UV irradiation at 20 min is shown in (d).

only 72.9 eV metallic Al peak was observed at 90 s. We cannot ascribe the absence of the 74.1 eV peak at 90 s to the dissociation of the adsorbates, because this interpretation contradicts the observation that the Al films grew more slowly under UV irradiation than without UV irradiation (Fig. 1). Instead, we propose that the adsorbates were lost partly by UV-induced desorption on the TiN surface, thus slowing down the Al growth.

The UV-induced desorption may offer an explanation for the reduced Al growth rate observed on TiN at 150 °C. Namely, the desorption competes with the dissociation, while their relative importance changes with temperature. Indeed, at 200 °C the UV-induced suppression was more prominent than in the present case.<sup>11</sup> This was observed on Si surfaces, but when Al was growing on Al underlayers the substrate surface should not have affected the outcome. At 120 °C the UV light helped to enhance the growth rate on Al.<sup>13</sup> These results suggested greater importance of the photoinduced desorption at higher temperatures.

Finally, Fig. 5 shows the Al 2p spectra taken for the TiON surface at the initial stage of the Al deposition. Even under UV irradiation the metallic Al signal was missing at 5 min. An identical peak was observed at 20 min without UV irradiation [Fig. 5(d)]. These results agreed with those obtained by the profilometer (Fig. 2). The peak observed at 75.1 eV is assumed to represent the adsorbates formed on

TiON, which shifted by 1.0 eV and therefore differed from those formed on TiN. The adsorbates formed on TiON cannot be dissociated so easily, even under UV irradiation, as those on TiN. Without UV irradiation they remained undissociated even at 20 min. The UV light helped to dissociate the adsorbates on TiON and form metallic Al at 10 min. An additional peak observed at 75.5 eV coincided with the signal we observed from  $Al_2O_3$ . The reduction of TiON was confirmed from the shift of Ti 2*p* binding energy back to 455 eV.

In summary, we studied Al film growth on TiN and TiON surfaces, using DMAH at 150 °C. Al films grew thermally at a rate of 6.3 nm/min on TiN, which was reduced to a lower rate of 5.2 nm/min under UV irradiation from the deuterium lamp. On TiON, Al did not start the growth without the UV light. XPS studies showed that the adsorbates formed on TiON differed from those on TiN. Part of the adsorbates formed on TiN was lost through photoinduced desorption, which explained the reduced growth rates under UV irradiation. On the other hand, the adsorbates formed on TiON could be dissociated only with the help of the UV light, as shown by the thickness and XPS studies.

We thank Kazuo Kawahito for technical assistance. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture.

- <sup>1</sup>R. Bhat, M. A. Koza, C. C. Chang, and S. A. Schwarz, J. Cryst. Growth **77**, 7 (1986).
- <sup>2</sup>O. Lehmann and M. Stuke, Appl. Phys. Lett. 61, 2027 (1992).
- <sup>3</sup>K. Sugai, T. Shinzawa, S. Kishida, and H. Okabayashi, Digest of Papers, 4th MicroProcess Conference, Kanazawa, Japan, 1991 (unpublished), pp. 206–207.
- <sup>4</sup>K. Sugai, H. Okabayashi, T. Shinzawa, S. Kishida, T. Kobayashi, N. Hosokawa, T. Yako, H. Kadokura, M. Isemura, and M. Naruse, *Proceedings of the Symposia on Interconnects, Contact Metallization, and Multilevel Metallization/Reliability for Semiconductor Devices, Interconnects, and Thin Insulator Materials*, edited by T. O. Herndon, K. Okabayashi, N. Alvi, H. S. Rathore, R. A. Susko, and M. Kashiwagi (Electrochemical Society, Pennington, NJ, 1993), Vol. 93-25, pp. 290–298.
- <sup>5</sup>K. Sugai, H. Okabayashi, T. Shinzawa, S. Kishida, A. Kobayashi, T. Yako, and H. Kadokura, J. Vac. Sci. Technol. B **13**, 2115 (1995).
- <sup>6</sup>M. Hanabusa, A. Oikawa, and Peng Ying Cai, J. Appl. Phys. **66**, 3268 (1989); **67**, 3208E (1990).
- <sup>7</sup>M. Eizenberg, MRS. Bull. XX (11), 38 (1995).
- <sup>8</sup>M. Hanabusa and M. Ikeda, Appl. Organomet. Chem. 5, 289 (1991).
- <sup>9</sup>D. Briggs and M. P. Seah, *Practical Surface Analysis*, 2nd ed. (Wiley, Chichester, 1990), p. 606.
- <sup>10</sup>M. Hanabusa and A. Komatsu, Appl. Surf. Sci. 86, 428 (1995).
- <sup>11</sup>T. Kawai, M. Okawa, A. Komatsu, T. Shimada, and M. Hanabusa, Appl. Surf. Sci. **79/80**, 385 (1994).
- <sup>12</sup>T. Kawai and M. Hanabusa, Jpn. J. Appl. Phys. 32, 4690 (1993).
- <sup>13</sup>T. Nitta, K. Nishitani, and M. Hanabusa, Jpn. J. Appl. Phys. 34, L1500 (1995).
- <sup>14</sup> M. Hanabusa and A. Komatsu, Appl. Phys. Lett. **65**, 1826 (1994).
  <sup>15</sup> Reference 9, p. 601.