Metal–organic atomic-layer deposition of titanium–silicon–nitride films

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Titanium–silicon–nitride films were grown by metal–organic atomic-layer deposition at 180 °C. When silane was supplied separately in the sequence of a tetrakis(dimethylamido) titanium pulse, silane pulse, and ammonia pulse, the Si content in the deposited films and the deposition thickness per cycle remained almost constant at 18 at. % and 0.22 nm/cycle, even though the silane partial pressure varied from 0.27 to 13.3 Pa. Especially, the Si content dependence is strikingly different from the conventional chemical-vapor deposition. The capacitance–voltage measurement revealed that the Ti–Si–N film prevents the diffusion of Cu up to 800 °C for 60 min. Step coverage was approximately 100% even on the 0.3 μm diam hole with slightly negative slope and 10:1 aspect ratio. © *1999 American Institute of Physics.* [S0003-6951(99)01137-7]

As the minimum feature size of semiconductor devices shrinks, the Cu diffusion barrier must be effective even when it is as thin as 10 nm because thick diffusion barriers leave little space for Cu, and thus, nullify the advantage of Cu metallization.[1,2] In this respect, more effective Cu diffusion barrier materials with a thinner thickness are required. Amorphous refractory ternary metals such as (Ti, Ta, W)–Si–N, W–B–N do not have fast diffusion paths such as a grain boundary present in polycrystalline materials and are promising candidates for these applications.[3,4] These diffusion barriers need to be deposited with good step coverage, especially on the sidewall, as the aspect ratio of contact/via/trench increases.

Metal–organic atomic-layer deposition (MOALD) achieves near-perfect step coverage and can control precisely the thickness and composition of grown films.[5] We have already demonstrated that TiN film could be grown with excellent conformality by MOALD using tetrakis(ethylmethylamido)titanium and NH_3.[6] However, MOALD of a ternary system may not be as easy to demonstrate as much as it is for a binary system and may not be understood straightforwardly in terms of chemical composition and growth kinetics. Therefore, in the present study, we have developed a MOALD technique for ternary Ti–Si–N films using a sequential supply of $Ti[N(CH_3)_2]_4$ [tetrakis(dimethylamido) titanium: TDMAT], silane (SiH_4), and ammonia (NH_3), and evaluated the Cu diffusion barrier characteristics of a 10 nm Ti–Si–N film with high-frequency small-signal capacitance–voltage ($C-V$) measurements.

A MOALD apparatus was used to grow Ti–Si–N films, which is schematically similar to the one described previously.[6] All the films were grown on SiO_2 (100 nm)/Si wafers at the substrate temperature of 180 °C and with the reactor pressure maintained at 133 Pa. TDMAT was delivered from the bubbler (30 °C) to the reactor using Ar (70 sccm) as a carrier gas. Also, the flow rates of NH_3 and SiH_4 (forming gas with 10% SiH_4/90% Ar) diluted in Ar were fixed at 70 sccm. The film thicknesses were measured by the surface profilometer. The composition of the grown film was analyzed using 9.0 MeV Cl^{5+} elastic recoil detection time of flight (ERD-TOF), 2.43 MeV He^{2+} Rutherford backscattering spectroscopy (RBS), and Auger electron spectroscopy (AES).

Figure 1 shows the dependence of the Si content in the Ti–Si–N film and the film deposition thickness per cycle on SiH_4 partial pressure. In this case, Ti–Si–N films were grown by a sequential supply of TDMAT for 5 s, SiH_4 for 10 s, and NH_3 for 10 s in a cyclic manner, and an Ar pulse for 20 s was inserted between each reactant gas pulse in order to isolate the reactant gases from each other. The partial pressure of SiH_4 was varied from 0.27 to 13.3 Pa by mixing with Ar. Despite the wide variation in SiH_4 partial pressure, the Si content in the films and the deposition thickness per cycle remain almost constant at 18 at. % and 0.22 nm/cycle, respectively. The dependence of Si content on the SiH_4 partial pressure in MOALD is quite different from the conventional metal–organic chemical-vapor deposition (MOCVD) of Ti–Si–N, in which the Si content in the film

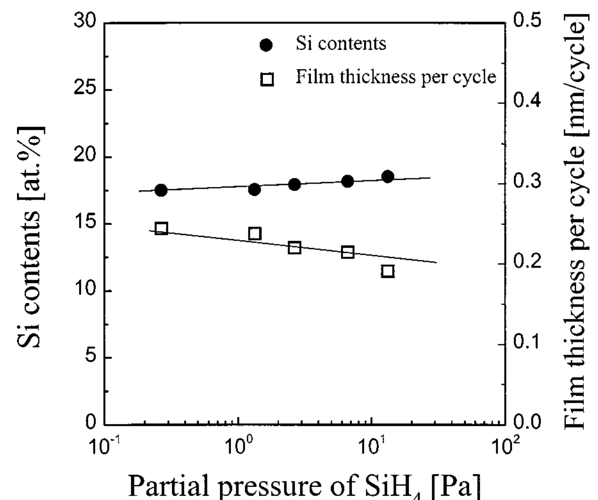

FIG. 1. Dependence of the Si content in the Ti–Si–N films and deposition thickness per cycle on the SiH_4 partial pressure for the films grown on SiO_2 at the substrate temperature of 180 °C. Ti–Si–N films were grown by sequential supply of TDMAT for 5 s, SiH_4 for 10 s, and NH_3 for 10 s.

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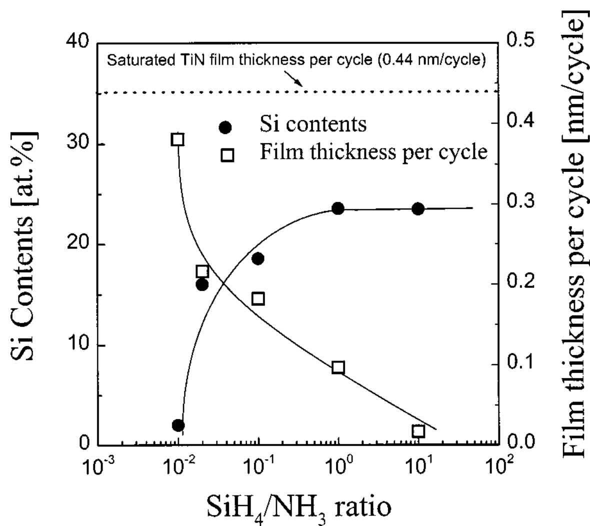

FIG. 2. Dependence of the Si content in the Ti–Si–N films and deposition thickness per cycle on the SiH_4/NH_3 ratio for the films grown on SiO_2 at the substrate temperature of 180 °C. SiH_4 and NH_3 were simultaneously supplied in the sequence of TDMAT for 5 s and SiH_4/NH_3 for 10 s. On the contrary, when TDMAT and NH_3 were alternately supplied without SiH_4, the saturated TiN deposition thickness per cycle was 0.44 nm/cycle.

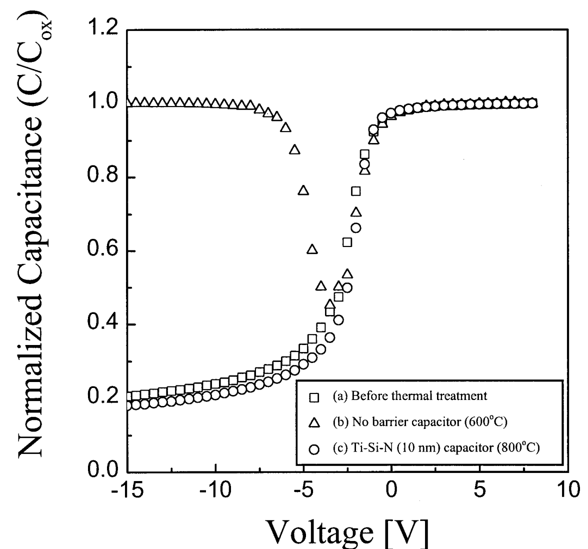

FIG. 3. 1 kHz $C-V$ measurements for MOS capacitors, Cu (100 nm)/10 nm Ti–Si–N barrier layer (or without the barrier layer)/SiO_2 (100 nm)/N-type Si. (a) and (b) are the $C-V$ profiles for the MOS capacitor without the barrier layer before and after thermal treatment at 600 °C for 60 min in H_2 (10%)/Ar (90%), respectively. (c) is the $C-V$ profiles for the MOS capacitor with a 10 nm Ti–Si–N barrier layer after thermal treatment at 800 °C for 60 min in H_2 (10%)/Ar (90%).

increases logarithmically as the partial pressure of SiH_4 increases.[7]

The difference between MOALD and MOCVD may originate from the fact that the Si content in the MOALD is controlled by the amount of SiH_4 that can be adsorbed on the surface during a SiH_4 pulse. As a preliminary experiment, it was observed that there was no reaction between SiH_4 and TDMAT, or SiH_4 and NH_3 at 180 °C. These results indicate that SiH_4 cannot react directly with TDMAT or NH_3 at this temperature. Thus, the amount of available adsorption sites for SiH_4 would be limited, since most of the available adsorption sites on the surface have been already occupied by TDMAT molecules, which were chemisorbed on the surface during the prior injection of the TDMAT pulse. Therefore, the Si content in the Ti–Si–N films will be controlled by the amount of SiH_4 adsorbed on the surface, not by the SiH_4 partial pressure.

On the other hand, the Ti–Si–N deposition thickness per cycle, 0.22 nm/cycle, is nearly half the value of TiN (0.44 nm/cycle, shown in Fig. 2). As mentioned above, SiH_4 cannot react directly with TDMAT or NH_3 at this MOALD temperature of 180 °C. Thus, SiH_4 can only take part in the Ti–Si–N formation during the reaction between TDMAT and NH_3. Therefore, when the substrate covered with both TDMAT and SiH_4 is exposed to the NH_3 pulse, the reaction between TDMAT and NH_3 should at first occur on the surface. And then, the SiH_4 adsorbed on the surface could be involved into the Ti–Si–N formation. But, excess SiH_4 would still remain on the surface after the end of the NH_3 pulse and act as a blockade toward the adsorption of TDMAT during the following TDMAT pulse of the next cycle. Consequently, the total quantity of TDMAT and NH_3 that contributes to the film growth during one cycle would be decreased, and it would result in reduction of the Ti–Si–N deposition thickness per cycle.

Figure 2 shows the dependence of the Si content and the deposition thickness per cycle on the SiH_4/NH_3 ratio. In this experiment, SiH_4 and NH_3 were simultaneously supplied in the sequence of the TDMAT pulse for 5 s and the SiH_4/NH_3 pulse for 10 s. The Si content increases as the SiH_4/NH_3 ratio increases and is saturated at 23 at. %. It is comparable to the conventional CVD that the Si content increases according to the SiH_4 partial pressure. The deposition thickness per cycle decreases continuously as the Si content in the film increases. Two possible reasons can be considered. The first reason is that the number of reactant molecules that contribute to the film deposition during one cycle decreases due to the SiH_4 blocking effect, as mentioned in Fig. 1. And the second reason is that the deficiency of NH_3 can also reduce the overall reaction rate during one cycle.

Metal–oxide–semiconductor (MOS) capacitors, Cu (100 nm)/barrier layer (or without the barrier layer)/SiO_2 (100

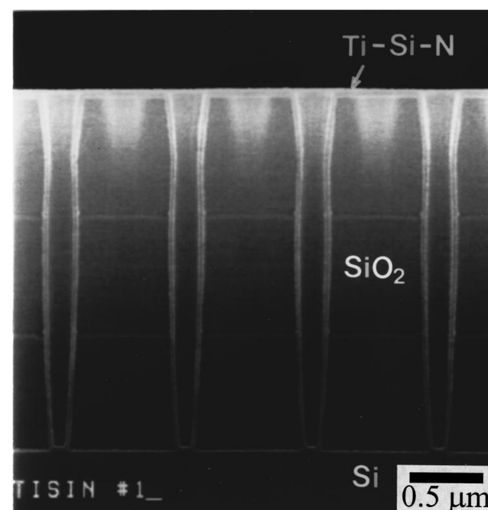

FIG. 4. Cross-sectional SEM micrograph of a 50 nm Ti–Si–N film grown by MOALD at 180 °C. Step coverage of the Ti–Si–N film is approximately 100% even on the 0.3 μm diam hole with slightly negative slope and 10:1 aspect ratio.

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nm)/*N*-type Si, were fabricated to investigate the Cu diffusion barrier characteristics of the MOALD Ti–Si–N film. Figure 3 shows the $C-V$ profiles measured at the 1 kHz frequency of a small signal. In Fig. 3, (a) and (b) are the $C-V$ profiles for the MOS capacitor without the barrier layer before and after thermal treatment at 600 °C for 60 min in H_2 (10%)/Ar (90%), respectively. (c) is the $C-V$ profile for the MOS capacitor with a 10 nm $Ti_{0.32}Si_{0.18}N_{0.50}$ barrier layer after thermal treatment at 800 °C for 60 min in H_2 (10%)/Ar (90%). In the case of (a), the $C-V$ profile shows the typical high-frequency small-signal $C-V$ characteristics. However, in the case of (b), the $C-V$ profile shows low-frequency $C-V$ characteristics in spite of the 1 kHz small-signal $C-V$ measurement. This will come from the Cu atoms diffused into the *N*-type Si, because Cu atoms form deep donor levels and can act as the generation and recombination centers of electron–hole pairs. But, in the case of (c), the $C-V$ profile shows no change by thermal treatment at 800 °C for 60 min, compared with the case of (a). It is revealed that the 10 nm Ti–Si–N film grown by MOALD performs the role of the Cu diffusion barrier up to 800 °C for the 60 min well.

The MOALD process has great potential for excellent step coverage on severe surface topography due to the complete surface reaction. Figure 4 shows the cross-sectional scanning electron microscope (SEM) image of the 50 nm Ti–Si–N film grown by the same method as in Fig. 1. It clearly demonstrates the perfect step coverage of MOALD even on the 0.3 μm diam hole with slightly negative slope and 10:1 aspect ratio.

A MOALD for Ti–Si–N was developed by alternate supply of TDMAT, SiH_4, and NH_3 at 180 °C. The MOALD Ti–Si–N films showed excellent Cu diffusion barrier performance with 10 nm thickness up to 800 °C for 60 min. MOALD is a promising deposition method for Ti–Si–N with less than 10 nm thickness as a Cu diffusion barrier film.

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