

IMPROVED CONFORMALITY OF CVD TITANIUM NITRIDE FILMS

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ABSTRACT

We demonstrate a novel approach to improving the step coverage of thin films made by chemical vapor deposition (CVD). Titanium nitride (TiN) films were deposited by atmospheric pressure CVD using tetrakis(diethylamido)titanium vapor (TDEAT) and ammonia gas (NH₃) carried in nitrogen gas. Trimethylamine (NMe₃) gas was added during some of the depositions. The substrates were patterned silicon wafers having holes with aspect ratio of 3.5 through a silicon dioxide layer. We discovered that the step coverage was significantly increased for TiN films made with NMe₃. At 320 °C, the step coverage was increased from 70% to nearly 100%. Within the range of deposition temperatures used in our study, 320 °C to 370 °C, the amount of improvement increased as the deposition temperature decreased. The trimethylamine did not increase the resistivity or the impurity levels in the films, but it did reduce the growth rate slightly. We suggest that the trimethylamine adsorbs onto the surface, temporarily blocking some of the sites on which growth could take place. Thus the effective sticking coefficients for the precursors are decreased, and the step coverage is increased.

INTRODUCTION

Chemical vapor deposition (CVD) is a very important technique in making thin films. One of the major advantages of CVD over physical vapor deposition (PVD) is that CVD can provide a much better conformality for films deposited on non-planar structure, which is required in many applications such as microelectronic device fabrication. For some applications even a step coverage as high as 80% may not be acceptable. For example, in tungsten plug fabrication, a step coverage of 80% could still leave a void in the plug, and cause device failure [1]. Therefore, techniques to make films of very high conformality are desirable.

TiN film has been extensively studied world wide because of its unique mechanical, chemical, electrical and optical properties. It is the standard material for adhesion layers, anti-reflective coatings and diffusion barriers in microelectronics industry. Currently, TiN films are deposited by sputtering. As device feature sizes are being further miniaturized, thinner TiN films are needed and will soon reach the limit of PVD capabilities. CVD TiN has been recognized as the most promising successor to PVD TiN because CVD TiN films can achieve much better step coverage, and also have a denser microstructure and thus may be better diffusion barriers [2].

In this paper, we propose a novel approach to improve step coverage of CVD films by control of their growth rate. Our approach was based on the fact that one of the most critical

determining the step coverage of CVD films are the sticking coefficients (S_c) of species involved in the deposition reaction [3]. S_c is defined to be the ratio of amount of material deposited on the substrate to the amount of material flowing onto the substrate. Lower S_c yields better (higher) step coverage. The most common way to reduce the S_c is to decrease deposition temperature and thus decrease deposition rate, at least for surface reactions having a positive activation energy [4]. A drawback of this kind of approach is a likely increase of film resistivity or/and impurities. In our approach to reducing S_c , instead of decreasing substrate temperature, another gas was introduced to decrease the sticking coefficient. By not decreasing the deposition temperature, increases of resistivity and impurities can be avoided.

Trimethylamine (NMe_3) was chosen to implement this method because it adsorbs very strongly on many surfaces and it should be non-reactive to the other chemicals involved in the CVD reaction. During TiN deposition, NMe_3 may adsorb on the TiN surface and cover part of the surface available for deposition of TiN, or increase the activation energy of the surface step in TiN deposition. NMe_3 may also form complexes with reactive gaseous intermediates, making them less reactive. Any of these effects would decrease the surface reaction rate, resulting in a smaller S_c and higher step coverage.

EXPERIMENTAL

TiN films were deposited in a Watkins-Johnson 956 belt furnace. Details of this apparatus can be found in a previous paper [5]; the only difference is that we added a NMe_3 gas line. Pure liquid TDEAT (99.999%, Schumacher) was vaporized at a controlled rate by an MKS-DLI-25 liquid delivery/vaporization system into a nitrogen carrier gas line which was heated up to 160 °C. From there it flowed down through two parallel slots onto the substrates. Semiconductor grade NH_3 (99.995%) and high purity NMe_3 (99.5%) from Matheson were purified through Nanochem resin purifiers, diluted with nitrogen carrier gas, heated to 160 °C and injected through a slot between the other two parallel slots. The N_2 carrier gas for TDEAT, NH_3 and NMe_3 was purified through an Oxiclear purifier and also heated up to 160 °C. The waste gases were exhausted through two parallel exhaust slots placed 10 cm apart.

The substrates were placed on a metal belt, passing first through a preheating zone and then through the deposition zone by the belt moving at a speed of 2 cm/min. The molar concentrations of TDEAT, NH_3 and NMe_3 were 0.010%, 1.0% and 0.68%, respectively, after mixing in the deposition zone. Experiments were conducted at preheating temperatures of 370 °C, 390 °C and 420 °C. Calibration runs were done using a thin thermocouple cemented to the surface of a test wafer. During the passage of the substrates through the reaction zone, the temperature of the test wafers dropped about 50 °C by heat transfer to the 160 °C gas distributor above the substrates. Thus we will use the measured substrate temperatures, rather than the preheat temperatures, to characterize the experimental conditions. At each temperature, control experiments without NMe_3 were conducted. Si wafers from Silicon Sense, soda lime glass from Kodak, and patterned SiO_2/Si wafers from Micron Technologies were used.

The composition of the films was measured by X-ray photoemission spectroscopy (XPS) using an SSX-100 ESCA Spectrometer made by Surface Science Laboratory. The films were sputtered with Ar plasma for 100 seconds before each XPS measurement. We carried out 5 sputtering-measuring cycles for each sample. The atomic percentages of the elements were determined by peak integration performed by the software package supplied with the XPS equipment. The film thickness and step coverage data were found using a LEO 980 Scanning Electron Microscope (SEM) pictures of the edges of cleaved substrates. The patterned wafers used for measurement of step coverage had 0.7 μm diameter cylindrical holes through a SiO_2 layer 2.4 μm thick on the Si substrates, corresponding to an aspect ratio of 3.5. Step coverage is defined as the ratio of TiN film thickness at the bottom of a hole to the film thickness on the top surface. The sheet resistance, R_s , was measured by a FPP-100 four-point probe made by Veeco Instruments, Inc. Film resistivity, ρ , was calculated by multiplying R_s by the thickness t from the SEM data.

RESULTS

Thickness and Growth Rate

All of the TiN films were uniform in thickness to a tolerance of about $\pm 5\%$. Considering that the length of the deposition zone in the direction of travel was 10 cm, the time that any particular region of substrate spent in the deposition zone was 4 minutes. The measured thicknesses were converted to the growth rates given in Table I. The addition of trimethylamine decreased the growth rate by 10 to 15%.

Table I. Growth rate, film composition and step coverage of some titanium nitride films

Temp (°C)	NMe ₃ conc (mole %)	Growth rate (Å/min)	Titanium (mole %)	Nitrogen (mole %)	Carbon (mole %)	Oxygen (mole %)	Step Coverage, %
320	0	175	48.8	32.5	5.6	13.1	70
320	0.68	150	49.4	32.1	4.0	14.5	100
340	0	200	48.7	33.0	5.9	12.3	35
340	0.68	180	48.7	33.4	4.9	13.0	45
370	0	235	49.1	35.8	5.0	10.1	25
370	0.68	210	48.9	34.1	5.7	11.2	30

Step Coverage

By adding NMe₃, the step coverage was significantly improved. At 320 °C, it increased from 70% without NMe₃, to nearly 100% with NMe₃. Figure 1 shows the SEM photographs, and Table 1 gives the derived step coverage values. The step coverage decreased as the deposition temperature increased, showing that there is an activation energy to the surface addition step. The amount of improvement in step coverage also decreased as the deposition temperature increased. At 370 °C, the step coverage was only improved from 25% to 30%.

Composition

Our measurements did not show any significant difference between the compositions of films made with or without NMe_3 , as shown in Table I. The carbon content was 4 to 6%, slightly above the background level for the XPS measurement, which was estimated to be about 2%. Changes of 1% in the carbon content could not be detected within the instrumental noise level.

As the deposition temperature increased, the nitrogen content increased slightly and the oxygen content decreased slightly. The titanium and carbon contents did not show any significant changes with deposition temperature.

Resistivity

There was no observable difference in resistivity between films made with or without NMe_3 . The resistivities were stable with air exposure following deposition, indicating a non-porous film morphology. However, the resistivities were generally high, >1000 ohm-cm, because of oxygen contamination during film growth. Resistivity decreased as the deposition temperature increased, because of the lower oxygen content of the films made at higher temperatures.

DISCUSSION

The step coverage is determined by the reactive sticking coefficient. A low sticking coefficient yields high step coverage. Trimethylamine could improve the step coverage by decreasing the reactivity of either the surface or the gaseous chemical species reacting at the surface.

We noted that the wafers emitted an odor of trimethylamine just after they were removed from the belt furnace. This suggests that trimethylamine adsorbs strongly onto the surface of the film. The adsorbed NMe_3 could block reactive sites on the surface, thereby lowering the sticking coefficient. This adsorption must be in dynamic equilibrium during the growth process, or some of the NMe_3 would have become trapped and buried in the growing film, increasing its carbon content. Since no increase in carbon content was detected, the NMe_3 must have been able to desorb before becoming covered by the growth of film around and over it.

The step coverage generally increases as the substrate temperature is lowered, presumably because an energy barrier exists between the reactive gaseous species and the surface sites onto which they attach. At lower temperatures, the average energy of a reactive molecule decreases, and its probability of surmounting the barrier decreases. Thus the sticking coefficient decreases at lower temperatures and the step coverage increases.

The adsorbed trimethylamine may increase the energy barrier to adsorption, thereby decreasing the adsorption probability and increasing the step coverage. Alternatively, the adsorbed NMe_3 might simply block some sites and leave the energy barriers to other sites unchanged. Still another possibility is that the NMe_3 may form complexes with gaseous species, reducing their reactivity with the surface. The present experiments are not able to distinguish between these possible mechanisms.

We did not increase the substrate temperature beyond 370 °C because the step coverage would decrease to values too small to be useful. Temperatures below 320 °C were not studied because the step coverage with NMe₃ was already increased to 100%. Since the step coverage is unlikely to increase further, measurements at temperatures below 320 °C would probably also give 100%. When vias with higher aspect ratios become available, then it would be reasonable to extend the measurements of step coverage to lower temperatures. So far, we have not done experiments at a fixed temperature with different NMe₃ concentrations. We hope to do these experiments in the future.

The oxygen contents of our films are high, for at least two possible reasons. First, the loading and unloading ends of our furnace are open to the air. Although we used more than 80 SLM N₂ flow for each end as curtain gas flow, oxygen might still be able to diffuse into the deposition zone. The concentration of the titanium precursor is only 0.01%, so even 10 ppm oxygen amounts to 10% oxygen impurity in the film, if the titanium and oxygen atoms are incorporated with the same efficiency. Second, since we used very large amount of “house” N₂ flow (>200 SLM total), it was not practical to purify all of it. We only purified the carrier gas for TDEAT, NH₃ and NMe₃. Some oxygen and water vapor in the house N₂ may diffuse into the deposition zone. A possible solution to these two problems is to seal the furnace better. And if the furnace is not open to the air, the high N₂ curtain flow would not be needed and it would be more practical to purify all the N₂ gas used. The oxygen content should also be reduced by growing the films more rapidly, using a higher titanium precursor concentration. By reducing the oxygen impurity levels of the films, their resistivity can be lowered considerably.[6]

CONCLUSIONS

By adding trimethylamine to the CVD atmosphere, the conformality of TiN films can be significantly improved. In the range of temperatures studied, the improvement increases as the deposition temperature decreases. At 320 °C, the step coverage of TiN films was increased from 70% to nearly 100% without increasing the resistivity or impurity levels of the films. This technique is very promising for making TiN films for diffusion barrier, anti-reflective and adhesion layers in microelectronic device fabrication. It also has potential for improving hard, corrosion-resistant coatings applied to other non-planar structures, such as cutting tools.

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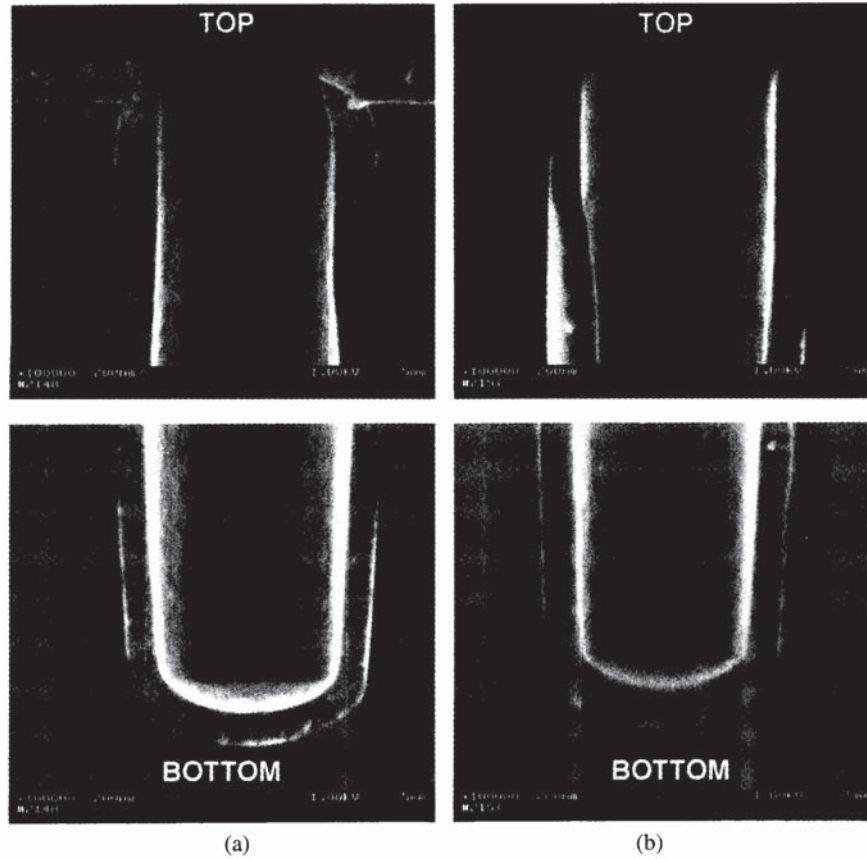


Figure 1. Tops and bottoms of cross-sectional SEM micrographs of titanium nitride coatings deposited at 320 °C over holes with aspect ratios of 3.5:1. a) without NMe₃ and b) with NMe₃.

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