Characterization of TiN films sputter-deposited at low temperatures

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Abstract

We have examined barrier deposition at low temperatures applicable to via last Cu-TSV. Among those, by changing the sputtering conditions, we successfully demonstrate in making two types of TiN films with different orientations. Even if the barrier material is the same, it has been demonstrated that the (200)-oriented TiN film has better barrier properties than the randomly oriented film in Cu/TiN/Si.

In this study, it is clarify whether orientation control of the TiN film can be obtained only on the Si substrate or on the SiO_2/Si substrate (namely on amorphous).

1. Introduction

TiN is well-known as a diffusion barrier with low resistivity (40-197 $\mu\Omega$ cm), but barrier properties are not satisfactory for Cu penetration at relatively high annealing temperatures.[1-4] In recent years, the TiN film is also being used as a barrier of Cu-TSV, but in this case, the deposition at low temperature of 200 °C or lower is required. It is generally known that the deposition temperature of the TiN film is 350-400 °C, when the deposition temperature at a lower than these, the sufficient barrier properties cannot be obtained.

In our previous study, we examined the TiN films deposited at low temperatures as diffusion barriers for via last Cu-TSV. Also, we examined the barrier properties of TiN on Si substrate, to facilitate the difference in properties. It is revealed that the TiN(200) orientation is good barrier properties compared with that randomly oriented film on Si substrate. [5]

In this study, to form the structure closer to Cu-TSV, we focused on the relationship between the orientation of the TiN films and their barrier properties on SiO_2/Si .

2. Experimental Procedure

TiN films (10-200 nm) were deposited on a p-type Si(100) substrate, SiO₂/Si substrate at 200 °C by reactive sputtering of a Ti target using an Ar + N₂ gas (15% or 30%) mixture. In some specimens, Cu films were prepared on the TiN/Si specimens using a tetrode dc sputtering system without breaking a vacuum. The target voltage and current of the TiN and Cu films were 1 kV and 80 mA, and 500 V and 70 mA, respectively. Total gas pressure was 2 x 10^{-3} Torr. Some specimens were annealed at 500 °C for 1 h in a vacuum of 10^{-7} Torr. X-ray diffraction (XRD), grazing in-

cidence X-ray reflectivity (GIXR), and X-ray photoelectron spectroscopy (XPS) were used to evaluate the crystallographic structure and/or texture, stack structure, and chemical state of the obtained samples.

3. Results and Discussion

Figure 1 shows the XRD pattern of the as-deposited TiN film (100nm) with different sputtering condition. In the case of using an Ar + N₂ (15%) gas mixture, a strong TiN(111) peak and weak TiN(200) peak, which show the polycrystalline phase with random orientation, are observed. On the other hand, in the case of using an Ar + N₂ (30%) gas mixture, only the TiN(200) peak is observed.

We have prepared a stack structure of Cu/(200)-oriented TiN (10 nm)/Si without insulating barrier to promote Cu diffusion. Figure 2 shows GIXR-measured curves of Cu/TiN (10 nm)/Si specimen using a TiN film deposited with an Ar + N_2 (30%) gas mixture (in blue) after annealing at 500 °C for 1 h. The calculation results (in red) fit well with the measured curves (in blue) in Figs. 2. Figure 3 shows schematic illustration of sample structure and model structure obtained from GIXR results. This GIXR result suggests the realization of the stacked structure without interfacial layers after annealing at 500 °C for 1 h in Figs. 3. Therefore, the obtained TiN barrier showed an excellent effect on the suppression of Cu diffusion and reaction without interfacial layers before and after annealing at 500 °C for 1 h. These results are in good agreement with the XRD analysis obtained from the Cu/TiN/Si system. On the other hand, in the randomly oriented TiN barrier, the reaction between Cu and Si could not be suppressed at 500 °C for 1 h, because the reflection lines of Cu₃Si were seen by XRD. From these results, it was revealed that even if the barrier material is the same, the barrier properties are different depending on the orientation of the barrier.

Figure 4 shows the XRD pattern of the obtained TiN film using an Ar + N₂ (30%) gas mixture on SiO₂/Si substrate. From XRD result, only the reflection peak from the slightly broad TiN(200) plane was obtained, but the intensity of the peak is slightly weak in comparison with that on the Si substrate. This is because that the film thickness of the TiN barrier on the SiO₂/Si substrate is very thin. Therefore, it was suggested that the orientation control of the TiN barrier is possible both on Si and SiO₂/Si.

4. Conclusions

We can prepare the low-temperature-deposited TiN films as a diffusion barrier for via last Cu-TSV. It was revealed that the (200)-oriented TiN film is obtained even on SiO_2/Si . The orientation of the obtained TiN barrier can be controlled by changing the sputtering conditions.

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Fig. 1 XRD patterns from the obtained TiN film using an $Ar + N_2$ (15 and 30%) gas mixtures on Si substrate.



Fig. 2 GIXR-measured curves of Cu/TiN (10 nm)/Si specimen using a TiN film deposited with an Ar + N_2 (30%) gas mixture (in blue) after annealing at 500 °C for 1 h. The calculated results are shown in red.





Fig. 3 Schematic illustration of sample structure and model structure obtained from GIXR results.

Fig. 4 XRD pattern of the obtained TiN film using an Ar + N_2 (30%) gas mixture on SiO_2/Si substrate.