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Application of Thin Nano-Crystalline VN Barrier in $Cu/VN/SiO_2/Si$ Systems

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1. Introduction

Thin diffusion barriers of less than 10 nm in thickness have been required to realize the Cu interconnects with line width of 0.1 μm or less in forthcoming Si-ULSI's[1]. Low-resistivity of materials is also favorable for a barrier applied to fine interconnects. To realize an ideal thin diffusion barrier using a continuous poly-crystalline film, we considered that the grain size of the barrier is significantly fine less than or comparable to the thickness of the thin barrier. It seems that the film consisting of larger size grains than its thickness results in a rugged interface and sometimes a discontinuous barrier. As a candidate for some such barrier materials, we attracted attention to a VN compound film, because V and N, the constituents of VN, have no reaction product with Cu and are scarcely soluble in Cu[2]. In the present study, we examined the barrier properties of VN layers consisting of nano-crystalline grains. The nano-crystalline VN barrier as thin as 10 nm in thickness was fairly stable without any chemical and/or structural instabilities at high temperatures up to 600°C or higher.

2. Experimental

Specimens of $Cu/VN/SiO_2/Si$ were prepared using a tetrode dc sputtering system with a base pressure of less than 3×10^{-7} Torr. On the SiO_2 layer (100nm) thermally grown on a p-type Si(100) wafer, a VN film (10nm) was deposited at 400°C by reactive sputtering using Ar + N_2 (30%) gas mixture. A Cu film (100nm) was then deposited on the VN layer at room temperature so as to complete the $Cu/VN/SiO_2/Si$ model system. The prepared specimens were then annealed at various temperatures up to 700 °C for 1 h in a vacuum of 10^{-7} Torr. The barrier properties and related reactions and/or diffusion taking place in the specimen upon annealing were characterizedby X-ray diffraction (XRD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and secondary ion mass spectroscopy (SIMS).

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3. Results and discussion

The prepared VN film was analyzed by AES, and the composition determined was $V_{0.45}N_{0.55}$. Any other AES signals such as from C or O contamination in the film were below the detectable limit. The XRD pattern obtained from the 100 nm thick VN film showed the very weak (111) and (200) reflection lines corresponding to a VN compound in a NaCl structure. The electrical resistivity measured for the ~200 nm thick film by the four-point probe method was about 50 μΩcm. This value is relatively low compared with those previously reported for films[3,4]. TEM observation indicated that the prepared VN film consists of several to ten nm grains. From the results described above, the present VN film is characterized by features of nitrogen-rich composition, low resistivity, and cubic structure consisting of nano-crystalline grains.

Figure 1 shows the compositional AES depth profiles obtained from the $Cu/VN/SiO_2/Si$ systems before and after annealing. The contamination by oxygen and carbon is below the detectable limit of the AES system throughout the obtained depth profiles, except at the surface of the specimen. Since the AES signal for Si atoms shows a change in energy and shape due to oxidation, we can show each distribution in the depth profiles depending on the chemical states. The depth profile obtained from the as-deposited $Cu/VN/SiO_2/Si$ system [Fig. 1(a)] shows the existence of Si at the VN/SiO_2 interface, suggesting a reduction of SiO_2 to the Si state at the interface even in the as-deposited system. From the XPS analysis of this specimen, chemical interaction between V and O, as well as the reduction of SiO_2 were confirmed at the VN/SiO_2 interface in the as-deposited system. This interfacial reaction is rather preferable to promote the adhesion of the VN barrier to SiO_2. Upon annealing at 600 °C for 1 h, the distribution of each element scarcely change in shape as seen in Fig. 1(b), indicating that the $Cu/VN/SiO_2/Si$ system is fairly stable due to annealing at 600 °C for 1 h without excess diffusion and/or reaction at each interface. In fact, the SIMS analysis for the above-mentioned specimens indicated an absence of Cu penetration into the SiO_2 or Si substrate through the VN barrier due to annealing.

Figure 2 shows the cross-sectional TEM view of the as-deposited $Cu/VN/SiO_2/Si$ system. As seen in the micrograph

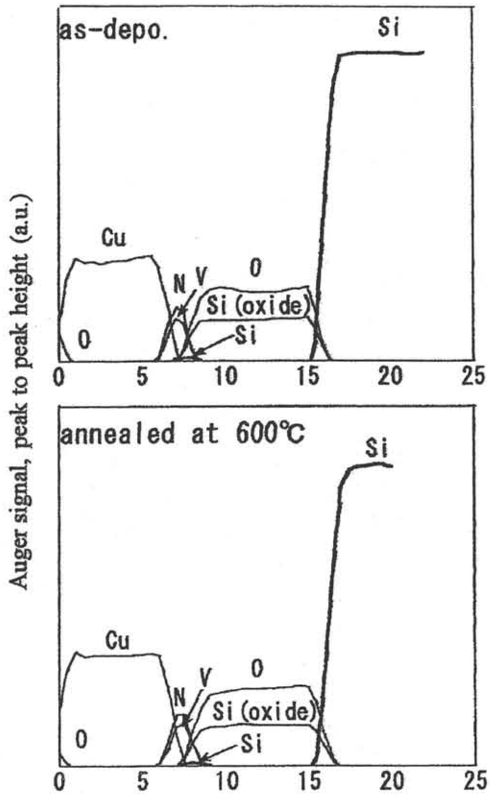

Fig. 1 AES depth profiles of the Cu/VN/SiO_2/Si system before and after annealing at 600 °C for 1 h.

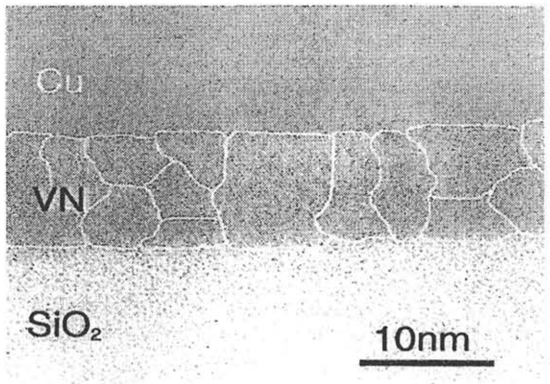

Fig. 2 Cross-sectional TEM micrograph of an as-deposited Cu/VN/SiO_2/Si system.

the VN barrier consisting of nano-crystalline grains is placed as a continuous film on SiO_2, on which the uniform Cu layer is observed to form a stacked structure. The Cu/VN and VN/SiO_2 interfaces are rather characterizedby the shape of the individual VN grain in the barrier. The features of the micrograph obtained from the specimen annealed at 600 °C for 1 h was scarcely changed from those in Fig. 2, although a slight growth of VN grains in the lateral direction was observed. The TEM observation also indicated the absence of solid-phase reaction at each interface due to annealing at 600 °C, which was consistent with the results of AES depth profiles as already seen in Fig. 1.

This feature is ascribed to the stability of the VN compound. The chemical state of VN is thermochemically advantageous as compared with any other chemical reactions forming other compounds possible in the present thin film assembly[5]. Furthermore, as mentioned above, the absence of Cu penetration through the barrier was also confirmed. The nitrogen-rich composition of the present VN barrier may result in the existence of stuffed nitrogen atoms at the grainboundaries of VN, which is favorable for preventing Cu penetration through the barrier. From the experimental results described above, the nano-crystalline VN barrier is a feasible material for application to the extremely thin diffusion barrier in the forthcoming Cu metallization technology.

4. Conclusions

We prepared the nano-crystalline VN film as a diffusion barrier as well as an adhesion-promoting layer interposed between Cu and SiO_2. We could successfully demonstrate the realization of a 10 nm thick thin diffusion barrier without excess solid-phase reaction and/or diffusion. The barrier prevented the Cu penetration at temperatures up to 600 °C or higher. The excellent barrier properties were ascribed to the chemical and structural stability of the prepared VN compound.

Acknowledgments

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