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Properties of barrierless Cu/ZrN_x/Si structure deposited at room temperature

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Abstract

We have examined Cu/ZrN_x/Si structure deposited at low temperature applicable to via last Cu-TSV. In this structure, no significant Cu diffusion was observed even after annealing at 500 ºC for 1 h, although there was no barrier metal for preventing Cu diffusion. Furthermore, having the excellent property that the insulating film deposited at room temperature can suppress the Cu diffusion at annealing temperature up to 500 ºC. without the diffusion barrier metal is a major stepping stone to the realization of via last TSV in the future.

1. Introduction

It is required that low-temperature insulating materials are useful for achieving low stress and high reliability in the via last TSV process.[1] We have been examined insulating materials that can be deposited at low temperatures below 200 ºC applicable to through silicon via (TSV).[2-4] In particular, Zr-N binary material has attracted attention. This is because the Zr-N binary system has low resistance ZrN and insulating Zr_3N_4. We have already proposed the combination of the low resistance ZrN and insulating Zr_3N_4, we can successfully prepare diffusion barrier and insulation barrier at low temperatures with the same components.[4] The obtained Cu/ZrN/Zr_3N_4/Si system was excellent thermal stability even at 500 ºC for 1 h.

On the other hand, in TSV, the concept of barrierless has been examined, which eliminates the diffusion barrier for preventing the diffusion of the Cu wiring. This means that if the insulating barrier film can also prevent the Cu diffusion, the area of the Cu wiring in the TSV can be sufficiently secured. Generally, the insulation barrier alone can not sufficiently suppress the diffusion of Cu, and a two-layer structure with the diffusion barrier metal is required.

In this study, we prepare a Cu/Zr_3N_4/Si structure without a ZrN film as a diffusion barrier metal and examine its thermal stability. Although this is a challenging examination, this barrierless structure shows a good thermal and structural stability in spite of depositing all layers at room temperature.

2. Experimental Procedure

Insulating ZrN_x films (~100 nm) were deposited on a p-type Si(100) substrate by RF reactive sputtering using a Zr target with an Ar + N_2 gas mixture. To form the Cu/ZrN_x/Si specimens, Cu films (~250 nm) were prepared on the ZrN_x/Si specimens in the same RF sputtering system using a Cu target with an Ar gas. The RF power of each of the ZrN_x and Cu films were 50W and 40W, respectively. All films were deposited at room temperature. Some specimens were annealed at various temperatures for 1 h in a vacuum of 3×10^{-6} Torr. X-ray diffraction (XRD), grazing incidence X-ray reflectivity (GIXR), transmission electron microscopy (TEM) with scanning transmission electron microscopy (STEM) and energydispersive X-ray analysis (EDX), and Fouriertransform infrared spectroscopy (FT-IR) were used to evaluate the crystallographic structure, the stack structure, and/or the chemical bonding states of the obtained specimens.

3. Results and Discussion

First, we will give an overview of our previous study. The thermal stability of the Cu/ZrN/Zr_3N_4/Si structure was examined. Here, the ZrN film is a conductive metal barrier and the Zr_3N_4 film is an insulating barrier. Figure 1 shows the STEM-HAADF image and corresponding EDX elemental mapping images of Zr and N of the Cu/ZrN/Zr_3N_4/Si structure before annealing. (already shown as Fig. 4 in ref. 4). In Fig. 1, the ZrN and Zr_3N_4 films are clearly different in contrast, indicating the difference in atomic composition between these films. This feature scarcely changes in images obtained from the specimen after annealing at 500 ºC for 1 h. However, the ZrN film was deposited at 200 ºC to promote the reaction between Zr and N atoms.

In this study, we examine the Cu/ZrN_x/Si structure excluding the barrier metal ZrN in order to obtain the two effects of securing sufficient area of the Cu wiring and sufficiently low temperature deposition for the via-last TSV process.

Figure 2 shows the XRD patterns of the ZrN_x film on Si substrate before and after annealing at various temperatures. In Fig. 2, a very broad peak corresponding to Zr_3N_4 is obtained from the as-deposited specimen. The XRD pattern hardly changes as the annealing temperature is increased. This implies that the obtained ZrN_x film has good thermal and structural stability without the grain re-crystallization owing to annealing. Also, we confirmed from the FT-IR data that there is no reaction between the obtained ZrN_x film and the Si substrate.

On the other hand, we show the XRD patterns of the barrierless structure of Cu/ZrN_x/Si before and after annealing as seen in Fig. 3. In the as-deposited specimen, a very broad peak corresponding to Zr_3N_4 is seen, in contrast to the sharp peaks from Cu. The annealing at 500 ºC for 1 h brings about the grain growth in only Cu film, and no reflection lines from additional reaction products are observed.

We performed GIXR measurements to confirm the change in configuration, especially the change in the obtained structure and/or the intermixing or reaction at every interface in the Cu/ZrN_x/Si specimen. The measured results are shown in Figs. 4(a) and 4(b) for specimens before and after annealing at 500 ºC for 1 h, respectively. These results suggest that the annealing data in scarce changes in structure and configuration in the stacked structure without interfacial layers. We will report on the utility of the insulating barrier deposited at room temperature, in addition to the other analyses results.

4. Conclusions

We can prepare the room-temperature-deposited ZrN_x films as an insulating barrier for via last Cu-TSV. The Cu/ZrN_x/Si structure shows a good thermal and structural stability. Also, a remarkable Cu diffusion is not observed even after annealing at 500 ºC for 1 h. These results indicate that the obtained ZrN_x is promising candidate for the insulating barrier applied to the via last TSV process.

Acknowledgements

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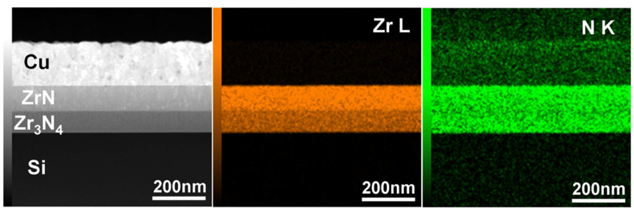

Fig. 1 STEM-HAADF image of Cu/ZrN/Zr_3N_4/Si specimen and corresponding EDX elemental images of Zr and N structure before annealing.

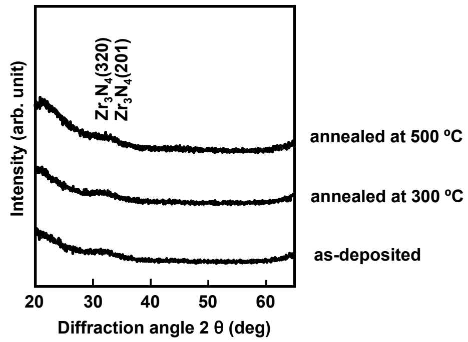

Fig. 2 XRD patterns of the ZrN_x film on Si substrate before and after annealing at various temperatures.

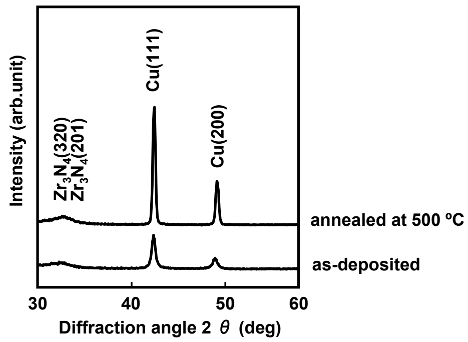

Fig. 3 XRD patterns of the Cu/ZrN_x/Si structure before and after annealing at 500 ºC for 1 h.

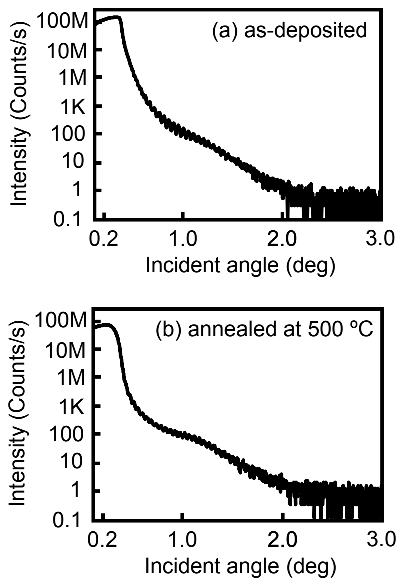

Fig. 4 GIXR-measured curves of Cu/ZrN_x/Si specimens: (a) before and (b) after annealing at 500 ºC for 1 h.