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Characterization of TiHfN ternary alloy films as a new barrier

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Abstract

In this paper, we propose a new ternary alloy nitride film of TiHfN as a candidate for a reliable barrier for Cu plug application. The TiHfN film consists of a single phase based on TiN or HfN, which are nitride of the same IVa group element with the same NaCl structure. We demonstrate TiHfN film with low resistivity (~120 μΩcm) in comparison of those of other ternary alloy films. The TiHfN film shows good barrier properties even after annealing at 700 °C for 1 h in the Cu/TiHfN/Si system. We report the characterization of the TiHfN films of various composition.

1. Introduction

TiN is well-known as a barrier of low resistivity (41-98 μΩcm), but its barrier properties are not satisfactory for Cu penetration at high temperature.[1-4] On the other hand, (Ta, W, or Mo)-Si-N ternary alloy barrier films show excellent thermal stability among barrier materials reported so far, but the resistivity of these films is extremely high(625-1800 μΩcm)[5-8], because of the amorphous phase.

We focus on the formation of the ternary alloy film with low resistivity. As its candidate, we pay attention to a TiHfN film, which consists of TiN or HfN phase with NaCl structure.[9] TiN and HfN are nitride of the same IVa group element, and also are low resistive materials. We expect that the TiHfN film is obtained as a low resistive barrier material.

In this study, we examine the characterization of TiHfN films with various composition. Also, we examine the barrier properties of TiHfN films in Cu/Si systems.

2. Experimental Procedure

TiHfN ternary alloy films (10-200 nm) were deposited on a p-type Si(100) or glass substrate at 400 °C by reactive sputtering of a Ti-Hf composite target using an Ar + N_2 gas mixture. In some specimens, Cu films were prepared on the TiHfN/Si specimens using a tetrode dc sputtering system without breaking a vacuum. The target voltage and current of the TiHfN 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 700 °C for 1 h in a vacuum of 10^{-7} Torr. X-ray diffraction (XRD), AES, and TEM were used to evaluate the crystallographic structure and/or texture, and composition of the obtained samples.

3. Results and Discussion

Figure 1 shows the XRD pattern of the TiHfN film. A broad reflection line with weak intensity is obtained at a 2θ value between HfN(200) and TiN(200) lines. In Fig. 1, the symmetric peak suggests that the prepared TiHfN film consists of a single phase based on that TiN or HfN in the NaCl phase. In a TiN-HfN system, it is expected that Ti and Hf atoms randomly substitute at cation sites in the lattice regardless of the local fluctuation in composition.

The composition of this TiHfN film determined by AES is $Ti_{12}Hf_{32}N_{56}$, a slightly N-rich composition. Here, both TiN and HfN are stable interstitial compound phases that can accommodate a considerable amount of excess nitrogen.

Figure 2 shows the variation of the lattice parameter in TiN-HfN system reported by Nowotny *et al*.[10] They reported that the lattice parameter of TiHfN film is nonlinear. In this study, the lattice parameters are 0.446 nm and 0.4466 nm deduced by XRD analysis and XTEM image, respectively, which are close to that (0.4467 nm) on the line in Fig. 2. It indicates that the TiHfN film is a composite of TiN and HfN with the random substitution of Ti and Hf atoms at cation sites. Moreover, we acquire a lattice parameter of the prepared HfN film with a slight N-rich composition. When we plot our data in Fig. 2, it is predicted that the lattice parameter becomes not nonlinear but linear. This difference seems to depend on difference in nitrogen content in the films.

The resistivity of this film (~200 nm in thickness) was ~120 μΩcm[9], which was sufficiently low as compared with those of ternary alloy films such as (Ta, W, or Mo)-Si-N amorphous films (625-1800 μΩcm).[5-8] Also, the resistivity of this thin film (~10 nm in thickness) was 320 μΩcm, which are low enough for their application as a thin barrier.

Figure 3 shows STEM-DF images and the corresponding EDS elemental mapping of the Cu/TiHfN(10 nm)/Si specimens before annealing and after annealing at 500 °C for 1 h. In Fig. 3, the remarkable diffusion of each element is not seen regardless of having the annealing or not. On the other hand, it is reported by Noya *et al*. that the Cu penetration is seen in Cu/TiN(100nm)/Si system after annealing at 500 °C for 1 h.[1] Good barrier properties of the TiHfN films are obtained by the alloying effect of TiN and HfN.

4. Conclusions

We propose the TiHfN films as a candidate for ternary alloy film with low resistivity. The TiHfN film with good characteristic that we expected is obtained. This is probably because Ti and Hf atoms in the TiHfN film can substitute at cation sites in the NaCl lattice. Also, Cu/TiHfN(10 nm)/Si contact tolerates even after annealing at 500 °C for 1 h, though the TiN barrier with 100 nm in thickness cannot suppress the Cu penetration. We will report the characterization of the TiHfN film of various composition.

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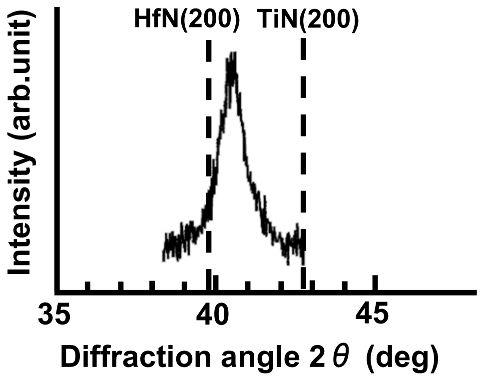

Fig. 1 XRD pattern of the obtained TiHfN film.

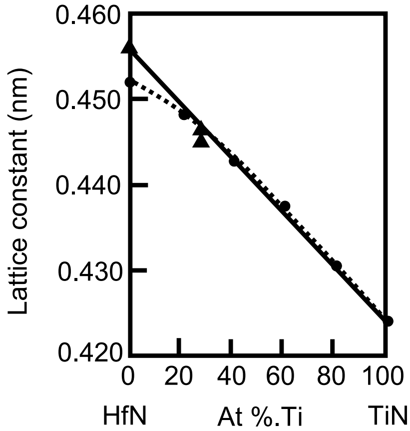

Fig. 2 Lattice parameter as a function of titanium content of the TiHfN film cited from Ref. 10: ▲, value in this study.

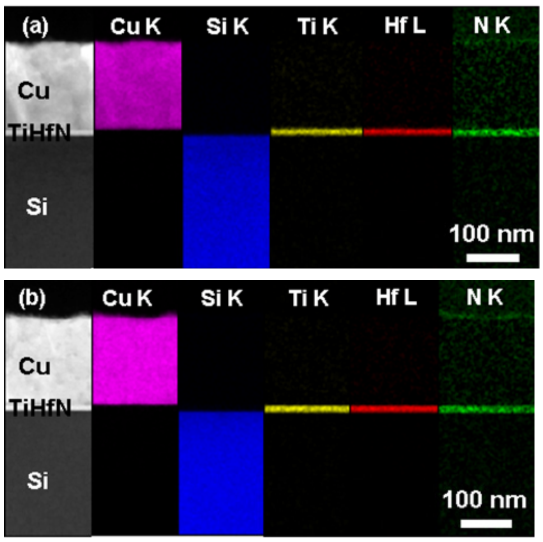

Fig. 3 STEM-DF images and the corresponding EDS elemental mapping of the Cu/TiHfN(10 nm)/Si specimens: (a) as-deposited and (b) annealed at 500 °C for 1 h.