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Effect of crystallinity and preferred orientation of Ta_2N films on diffusion barrier properties for copper metallization

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Abstract

Tantalum nitride (Ta_2N) films deposited at various substrate temperatures onto silicon (001) substrates can produce amorphous and crystalline phase with different preferred orientations. Subsequently, the viability of employing them as the diffusion barriers between copper and silicon is investigated by annealing at various temperatures for 30 min. The characterization of the thin films was carried out by four-point probe and X-ray diffraction. The results indicate that the thermal stability of Ta_2N with Cu and Si are dependent on the crystallinity of Ta_2N. Ta_2N phase with the highest (002) preferred orientation exhibits the highest structural stability to prevent copper diffusion more effectively.

Keywords: Tantalum nitride; Preferred orientation; Diffusion barrier; Annealing

1. Introduction

Copper has been the most promising wiring material for ultra-large scale integration (ULSI) devices [1] because Cu has the lower electrical resistivity of 1.67 μΩ cm and higher resistance to electromigration compared with Al or Al alloys [2,3]. However, the most serious problem about Cu is its fast diffusion in Si and the resulting highly resistive Cu_3Si compound, which degraded the reliability of the ULSI devices during post-annealing. Therefore, a better diffusion barrier layer to prevent the interdiffusion or reaction between Cu and adjoining materials is necessary.

The choices of barrier layers have been ranging from amorphous-materials, pure-metals and nitride-metals. The best materials of them were refractory metals, such as Tantalum (Ta), and the most effective way to prevent Cu interdiffusion was achieved by incorporating a second element, such as N or Si. Consequently, Ta–N systems including Ta, Ta_2N and TaN [4–10] have been selected as the barrier layers in the current technology. Generally, the failure mechanisms of Cu/TaN/Si structures can be classified into two types: (1) copper diffusion into silicon though the TaN barrier layer to form Cu–Si compounds (Cu_3Si); (2) the TaN diffusion barrier reactions with silicon to form Ta–Si compounds ($TaSi_2$) [11]. However, the failure mechanism of a Ta_2N layer as the barrier is unclear, even though some studies have indicated that the degradation of the Ta_2N layers is largely caused by decomposition to form Ta–Si compounds at high temperatures, followed by Cu–Si compounds [12]. Moreover, the role of the initial crystallinity in the diffusion barrier layer for the same phase has not been examined yet.

There is a strong correlation between the microstructure of barrier layers and atomic diffusion across the barrier. The microstructure variables include vacancy, dislocation, grain boundary, preferred orientation and crystallinity. However, there is no report on the comparative study of each crystalline variable for Ta_2N. In this article, we first show amorphous Ta_2N and (002) preferred orientated crystalline Ta_2N can be prepared by varying growth temperature during sputtering. Subsequently, we discuss the influence of the crystallinity of the Ta_2N films on the thermal stability upon annealing. The results indicate that the (002) oriented crystalline Ta_2N films can act as an excellent diffusion barrier against Cu diffusion up to 800 °C.

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2. Experimental details

A reactive RF magnetron sputter was employed to deposit Ta_2N thin films with N_2 on n-type Si(001) substrates. The target is Ta of 99.95% in purity, which was pre-sputtered for 5 min after the base pressure of 3×10^{-6} Torr was reached. The working pressure was fixed at 7×10^{-3} Torr, while the total gas (N_2+Ar) flow was maintained at 100 sccm. The gas flow ratio and substrate temperature were varied to examine the crystallinity and phase evolution of the Ta–N compound. Ta_2N thin films were then selected for the studies of the diffusion barrier properties for the Cu metallization in ULSI devices upon annealing in the structure of Cu (150 nm)/Ta_2N (100 nm)/Si. The Ta_2N diffusion barriers examined include amorphous and crystalline Ta_2N, deposited at room temperature, 100 °C and 200 °C. The specimens were then ex-situ annealed at various temperatures up to 800 °C for 30 min in a vacuum tube of 3×10^{-5} Torr, where the heating and cooling rates were set to be 10 and −26 °C/min, respectively. On the characterization side, the sheet resistance of the films was measured by four-point probe (FPP), and X-ray diffraction (XRD) was employed to determine the phase of the thin films, while the copper surface morphology was inspected by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Phases of the as-deposited Ta–N thin films

Fig. 1 shows a Ta–N phase diagram representing the resulting phase dependence of growth conditions, which integrate results from FPP, XRD and X-ray photoelectron spectroscopy (not shown). The sequence of the phase formation with $N_2/(Ar+N_2)$ ratio for a given substrate bias is poly-Ta, amorphous Ta_2N, poly-TaN, and poly-Ta_4N_5. In general, the electrical resistivity of the TaN_x films increases with increasing $N_2/(Ar+N_2)$ ratio and slightly decreases with substrate bias. Therefore, the highest electrical resistivity of Ta_4N_5 is obtained using $N_2/(Ar+N_2)$ ratio and substrate bias of 2.5% and −100 V, respectively. When deposited with a range of $N_2/(Ar+N_2)$ ratio from 1% to 2% at the substrate bias of −140V, TaN phase possesses approximately constant resistivity of 210 μΩ cm, which is close to that of TaN bulk. We also observed that there are regions between the single phase of TaN and Ta_2N, where these two phases coexist. Moreover, amorphous Ta_2N phase (a-Ta_2N) can be synthesized with the $N_2/(Ar+N_2)$ ratio of 0.5% and the substrate bias of −140 V at room temperature as shown in Figs. 1 and 2(a). Using exactly the same conditions, subsequently, a series of Ta_2N films were deposited at the growth temperature from 25 to 200 °C. The phases of the Ta_2N capped with Cu as a function of deposition temperature is shown in Fig. 2 from XRD. Apparently, with increasing deposition temperature, the degree of the Ta_2N crystallinity increases from amorphous at room temperature to 100% crystalline at 200 °C, where the Ta_2N is of (002) preferred orientation. Hereafter, the Ta_2N deposited at 100 °C and 200 °C are denoted as Ta_2N(A) and Ta_2N(B), respectively.

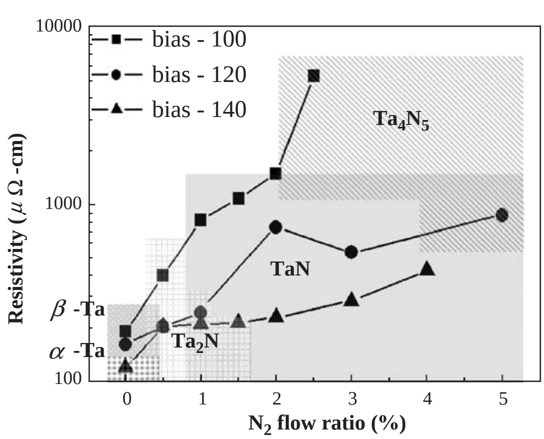

Fig. 1. Resistivity of the Ta and Ta–N films with various $N_2/Ar+N_2$ ratios.

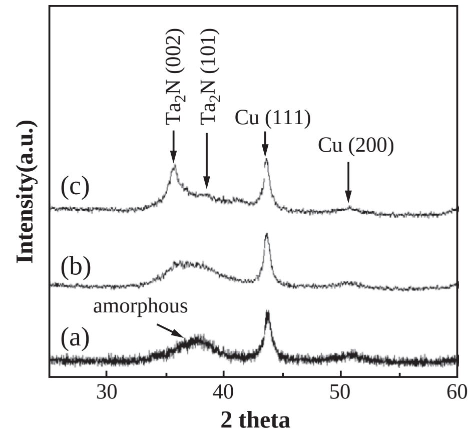

Fig. 2. X-ray diffraction patterns of the as-deposited (a) Cu/a-Ta_2N/Si at RT, (b) Cu/Ta_2N(A)/Si at 100 °C and (c) Cu/Ta_2N(B)/Si samples at 200 °C.

3.2. Diffusion barrier properties of Ta2N

Three Ta_2N films with different crystallinity are compared for the diffusion barrier properties in Cu/Ta_2N/Si. Fig. 3 shows sheet resistance with respect to annealing temperature from three Cu/Ta_2N/Si samples with different Ta_2N crystallinity. The variation of sheet resistance mainly reflects the changes in the thickness, integrity or chemical stability of the reacting copper layer. This is attributed to that the resistivity of copper is remarkably smaller than that of Ta_2N and silicon. Sheet resistance of the Cu/a-Ta_2N/Si structures, as shown in Fig. 3(a), decreases slightly at 500 °C, which is due to both grain growth and defect annihilation. Subsequently, sheet resistance remains almost the same up to 700 °C. As the temperature exceeds 700 °C, sheet resistance of the sample rises abruptly, indicating that severe elemental intermixing and probably new compounds have occurred