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Improved diffusion barrier performance of Ru/TaN bilayer by N effusion in TaN underlayer

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HIGHLIGHTS

► Success synthesis of two bilayers of Ru/N-unsaturated and N-supersaturated TaN.
► RuN exists in Ru/N-supersaturated TaN after annealing at 650 °C.
► Ru/N-supersaturated TaN exhibits high thermal stability.
► N effusion from TaN underlayer is responsible for the high thermal stability.

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ABSTRACT

Two bilayers of Ru/TaN with low N concentration and high N concentration (TaN_L and TaN_H) were used to determine the effect of N effusion on the barrier property. The results show that Ru/TaN_H bilayer exhibits a better barrier property, in which RuN existed even after annealing at 650 °C. The improved barrier property is attributed to the formation of RuN and N atoms stuffing in grain boundaries of Ru layer by sufficient effusion N atoms from TaN_H during annealing.

1. Introduction

Cu interconnect in integrated circuit (IC) requires an effective barrier to prevent interdiffusion or reaction between Cu and adjoining materials [1–3]. When the line width is reduced to nanometer regime in IC, barrier materials are occupying an increasing fraction at the cross-sectional area of conductors [4]. Thus, an ultra-thin Cu diffusion barrier with excellent barrier performance and low interconnect resistivity is needed to enhance IC performance [5]. Recently, Ru emerged as a promising barrier material due to low bulk resistivity (7.1 μΩ cm) and very low solubility with copper [6]. More importantly, Ru is an excellent barrier for direct Cu electroplating without the need of an additional Cu-seed layer, which will simplify the process and reduce fabrication cost [7–10].

Despite these merits, Ru is not a suitable diffusion barrier against Cu mainly due to its poor microstructure with polycrystalline columnar grains and poor adhesion to SiO_2-based dielectric material [11–13]. Hence, it is very important to improve the barrier property of Ru film. Better barrier performance of RuN than that of the pure Ru was reported by many researchers. Damayanti et al. reported that these advantages can be attributed to the N atoms dissolved and stuffed in the grain boundaries (GBs) of Ru films. Unfortunately, RuN is known to be decomposed after annealing at 275 °C [14,15]. Consequently, enhancing thermal stability of RuN becomes critical for improving the barrier performance of Ru film. In this letter, we propose a method for fabricating a Ru/TaN bilayer by means of introducing TaN underlayer with low N concentration and high N concentration, named as TaN_L and TaN_H. A better barrier property of Ru/TaN_H bilayer was found and the corresponding mechanism was also discussed.

2. Experimental

Cu/Ru/TaN stacks were deposited on the Si substrates by magnetron sputtering. After cleaning in an ultrasonic bath with alcohol for 30 min, the substrates were immediately loaded into the vacuum chamber. The base and working pressure of the sputtering

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chamber was 2×10^{-4} Pa and 1.2 Pa, respectively. TaN_L and TaN_H films of about 8 nm were obtained by adjusting the N flow rate. On the top of the TaN film, a Ru film of about 8 nm and a Cu film of 200 nm thickness were subsequently deposited to gain a Cu/Ru/TaN/Si stack. All targets were pre-sputtered before deposition to remove contaminants. No intentional heating was applied to the substrates during deposition. More details about the deposition system employed in this work are available in previous research [16–19]. Stacks were postannealed in a vacuum of 1×10^{-4} Pa at different temperatures for 30 min.

X-ray diffraction (XRD) system (Rigaku, Ultima-III) was used to characterize the texture and thermal stability of the thin films. The sheet resistance (SR) of Cu/Ru/TaN/Si stacks was measured at room temperature with a four-point probe measurement system (SB 120/2). The composition, chemical state and interface diffusion of the stacks were determined by X-ray photoelectron spectroscopy (XPS) (Thermofish, K-alpha). Transmission electron microscopy (TEM) was employed to observe the cross-sectional microstructure of stacked film.

3. Results

Fig. 1a displays the binding energy (BE) of Ta 4p3/N 1s peaks of Ta and TaN with the variation of N flow rates. The chemical shift from Ta to TaN reveals the fact that Ta atoms were in different valence states. The spectra have five significant points which can be referred to three Ta and two N binding states, as indicated in Fig. 1a [20]. The XPS spectrum for Ta shows the overlap of Ta–O and Ta features with a broad peak at binding energy of 400–406 eV. With the continuous increase in N flow rate, the Ta 4p3/N 1s signal intensity increases, which is attributed to the formation of Ta–N bindings. Moreover, a shift of Ta 4p3 peak from Ta–O to Ta–N can be also observed. While no appreciable changes are seen in N 1s spectra, suggesting oxygen is replaced by nitrogen during nitridation. The corresponding Ta/N ratio is seen in the inset of Fig. 1a. The initial ratio of Ta/N about 0.46 decreases to approximately 0.33 and then becomes stable despite of increasing N flow.

From the above results, we choose N_2 flow rates of 3 and 7 sccm for depositing TaN_L and TaN_H underlayer, respectively. Fig. 1b plots the ΔR variation versus annealing temperatures for the Cu/Ru/TaN/Si structures. ΔR is evaluated as $R-R_0$, which denotes the difference between resistivity before and after annealing. Unlike Ru/TaN_H bilayer, the $\Delta R/R_0$ of the Ru/TaN_L bilayer increases abruptly when the temperature is above 550 °C. XRD analysis obtained at and below 550 °C indicates only diffraction peaks from Cu without Ru or Ru_2Si_3 peaks (Fig. 1c,d). Above 650 °C, additional new peaks appear associated with the formation of Cu_3Si and Cu_4Si phase, as indexed in Fig. 1c [21]. Cu_4Si phase becomes dominant in Cu/Ru/TaN_L/Si, while Cu remains as the major phase without peaks linked to Cu_3Si or Cu_4Si in Cu/Ru/TaN_H/Si. Both $\Delta R/R_0$ and XRD results suggests that the Ru/TaN_H stack has a better thermal stability compared with the Ru/TaN_L. TaN barrier layer with 5–20 nm thickness has high thermal stability from 500 to 700 °C [3,22,23]. However, Ru barrier layer is not a very effective diffusion barrier for copper, which is destroyed after annealing at 300–500 °C [6,9,24,25]. In the present work, the thermal stability of Cu/Ru/TaN/Si stack is significantly superior to Cu/Ru/Si structure. Therefore, incorporation of TaN underlayer between Ru and Si effectively delayed the Cu atom diffusion. There are two reasons for it: (i) Amorphous TaN is thought to provide improved barrier performance due to the absence of GB for fast Cu diffusion. (ii) The effusion N atoms stuff at the GBs of Ru layer, which effectively block the pathways of Cu diffusion.

Fig. 2 presents XPS depth profiles of Ru/TaN for as-deposited stacks and those annealed at 650 °C. As displayed in Fig. 2a,b, the interfaces of as-deposited Ru/TaN stacks are distinguished. Additionally, there is very high oxygen content in the TaN layer as compared with Ru layer. The oxygen signal detected in TaN layer

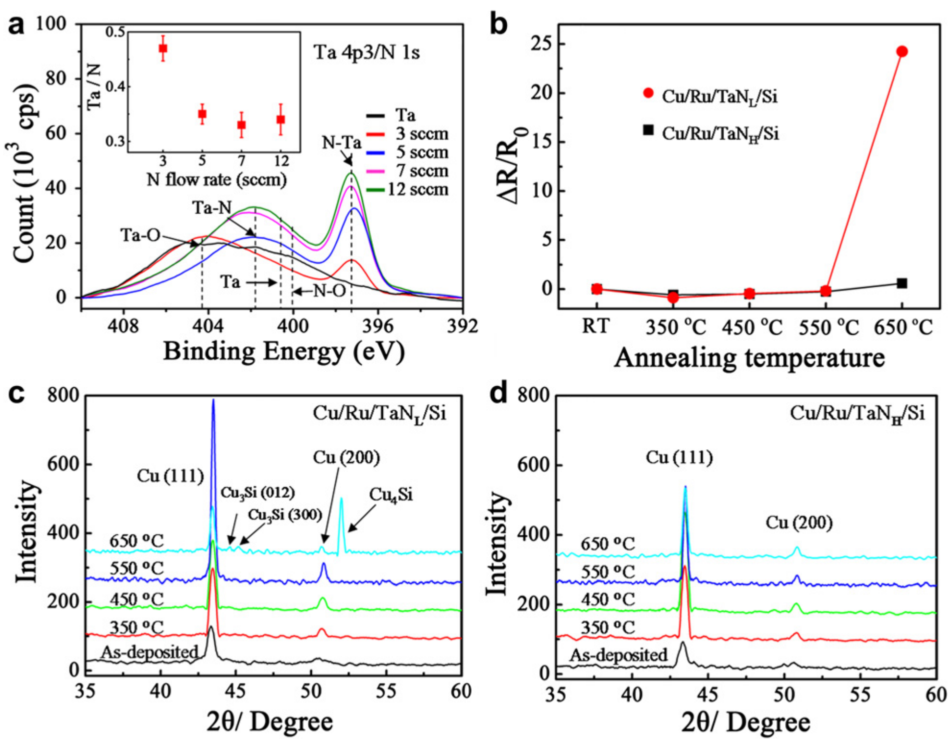

Fig. 1. (a) Change of the chemical states of the Ta 4p3 and N 1s signals of Ta and TaN with different N flow rates; The inset shows the change of Ta/N ratio with the variation of N flow rates (b) Evolution of the $\Delta R/R_0$ as a function of annealing temperatures (c and d) XRD patterns of Cu/Ru/TaN/Si stacks including as-deposited and annealed at different temperatures for 30 min.