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Study of ultrathin vanadium nitride as diffusion barrier for copper interconnect

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Abstract

Ultrathin Vanadium nitride (VN) thin film with thickness around 10 nm was studied as diffusion barrier between copper and SiO_2 or Si substrate. The VN film was prepared by reactive ion beam sputtering. X-ray diffraction, Auger electron spectroscopy, scanning electron microscopy and current–voltage (*I–V*) technique were applied to characterize the diffusion barrier properties for VN in Cu/VN/Si and Cu/VN/SiO_2 structures. The as-deposited VN film was amorphous and could be thermal stable up to 800 °C annealing. Multiple results show that the ultrathin VN film has good diffusion barrier properties for copper.

Keywords: Diffusion barrier; Copper interconnect; Vanadium nitride

1. Introduction

The transition metal nitrides have been the subject of intensive studies due to their superior characteristics, such as high melting point, hardness and metallic resistivity. Many nitrides have been widely studied because of their application in microelectronics, such as TiN [1], TaN [2], WN [3], Ti–Si–N [4], Ta–Si–N [5] and W–Si–N [6], which are excellent diffusion barriers in copper interconnect systems.

The VN film is very hard and has got wide application as hard coatings in mechanical apparatus. It is a kind of superconductor and got hot research in 1980s [7,8]. Its resistivity at room temperature is about 100 $\mu\Omega \cdot$ cm, depending on the deposition method and the film composition [7]. There are a lot of methods to prepare VN thin films, such as sputtering the VN film from a compound target [9], using reactive pulse laser deposition (PLD) method [10], and reactive magnetron sputtering [11], etc. It was reported that polycrystalline δ-VN film can be formed by rapid thermal annealing of V layer in N_2 after annealing at temperature higher than 900 °C for 10 s [12]. VN_x films can be formed by PLD in N_2 and H_2 ambient and its formation temperature is critical. By using reactive magnetron sputtering, different VN phases can be formed by varying the N_2 partial pressure. These reports are mainly on VN formation and its composition variation with deposition condition. Here, we report our effort to investigate the ion beam sputtered VN film as diffusion barrier to copper.

As we know, Cu diffuses very fast in Si and SiO_2 and will result in deep level trapping in the Si band gap. It may seriously degrade the electronic devices. An ultrathin and robust diffusion barrier compatible with modern copper technology is necessary. The VN film, a refractory nitride which has high melting point and low electrical resistivity, seem fit for the basic diffusion barrier requirement. Our results show that the VN film is a good diffusion barrier for copper.

2. Experimental

N-type Si (1 0 0) wafers with resistivity of 5–8 $\Omega \cdot$ cm or oxidized Si wafers were used as starting substrates. After a standard RCA cleaning process, the wafers were loaded

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into an Oxford sputtering system. The base pressure is about 7×10^{-5} Pa. The VN film was deposited by reactive ion beam sputtering by introducing N_2 into Ar atmosphere. The Ar to N_2 ratio was fixed at 2:1. The total working pressure was about 5×10^{-3} Pa. VN and copper thin films were sequentially deposited. Then the as-deposited samples were cut into small pieces. Rapid thermal annealing (RTA) for the VN films and the Cu/VN/Si samples was performed at temperatures from 300 to 900 °C for times ranging from 1 min to several hours in high purity N_2 ambient.

A four-point probe was used to measure the sheet resistance of the films. Phase identification of the layer was characterized by X-ray diffraction (XRD). Atomic redistribution during RTA was investigated by Auger electron spectroscopy (AES) depth profiling. The morphology of the film was observed by field-emission scanning electron microscopy (SEM). For measuring the copper diffusion in the oxide, a Cu gate MOS structure was made by lift-off method. After annealing, the backside Ti/Al layers were deposited as ohmic contact. Current–voltage (*I–V*) measurement was carried out . The oxide thickness is 100 nm.

3. Results and discussion

3.1. VN/SiO_2 structure

The as-deposited VN film had a brown color. The sheet resistivity of the film was about 400 μΩ · cm. Fig. 1 gives the sheet resistance variation for the film with annealing temperature. For comparison, the sheet resistance of the as-deposited film is also shown in Fig. 1. It shows that annealing at the temperature range of 400–800 °C does not cause significant resistance change for the film. Annealing results in slightly decrease of sheet resistance of the film. This may be due to the grain growth during the annealing.

Fig. 2 shows the XRD spectra for the VN(~100 nm) film on SiO_2 substrate after annealing at different temperatures. There is no obvious diffraction peak in the XRD spectrum for the as-deposited film. As we know, pure V

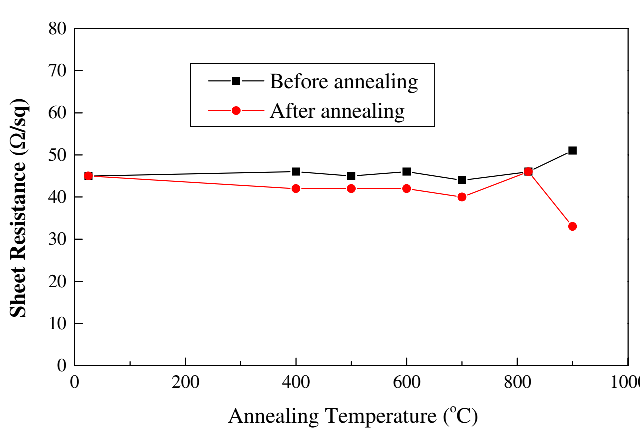

Fig. 1. The variation of sheet resistance for the VN(~100 nm)/SiO_2 samples with annealing temperatures.

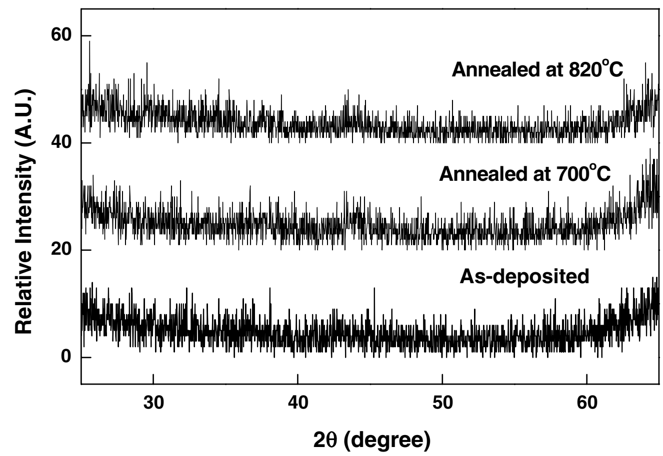

Fig. 2. The XRD spectra for the VN(~100 nm) film on SiO_2 substrate after annealing at different temperatures.

has a bcc structure with lattice parameter of 3.03Å. Normally, thin film directly deposited from the metal target will have a polycrystalline structure and has strong XRD peak. Therefore, from this figure we can know that no V phase can be found in the film, indicating that N has been successfully incorporated with V during the reactive ion beam sputtering and the formed thin film is amorphous. After annealing at 700 and 820 °C, no significant change can be observed. The VN film still keeps the X-ray amorphous structure. This result demonstrates superior thermal stability for the ion beam sputtered VN thin film.

3.2. Cu/ultrathin VN/Si structure

For study the diffusion barrier properties, ultrathin VN film with thickness of about 10 nm was deposited on Si and then copper was sequentially deposited onto it. Before annealing, the sheet resistance of each sample was measured (recorded as R_s). After annealing, the sheet resistance of the sample was measured again and was recorded as R_f.

Since the diffusion barrier is very thin, the sheet resistance of the Cu/VN/Si structure mainly reflects the resistance of Cu. The difference of sheet resistance between the annealed and as-deposited samples ($R_f - R_s$), divided by the sheet resistance of as-deposited samples, is called the variation percentage of sheet resistance [13]. Fig. 3 presents the variation percentage of sheet resistance versus annealing temperature for the Cu(100 nm)/VN(10 nm)/Si structure. It shows that after annealing up to 750 °C, the variation percentage is negative which is caused by reduced resistivity after annealing due to copper grain growth. Annealing at 825 °C causes the increase of the percentage to 2. Annealing at 850 °C results in the rapid increase of this percentage, indicating the significant interdiffusion of Cu and Si. For comparison, the Cu/VN/Si samples with VN thickness of 10 nm were also undergone 550, 600 and 650 °C annealing in N_2 for half an hour. The results show that the film can be stable up to annealing at 600 °C for at least half an hour. Annealing at 650 °C for half an hour has