Thin HfSiN Films prepared by Magnetron Sputtering

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Keywords: HfSiN thin films; magnetic sputtering; HfSiN/Cu/HfSiN/SiO2/Si

Abstract. HfSiN thin films were prepared by the solid solution of HfN and SiN precursor films through magnetron sputtering. The obtained films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray diffraction(XRD) measurements show that the films have amorphous structure in the as-deposited state. Scanning electronic microscopy (SEM) images show that crystalline grain size of the films increases with the annealing temperature. The results show that the resistivity and the components of the HfSiN/Cu/ HfSiN/SiO2/Si film do not have obvious change after being annealing at 550˚C in oxygen, and the HfSiN film can provide good barrier performance for copper wire.

Introduction

Copper has been extensively studied as an interconnect material for deep sub-micron circuits due to its superior electrical resistivity and resistance to electromigration. A suitable diffusion barrier is crucial to suppress the diffusion and reaction taking place between copper and silicon at low temperature for realizing thermally stable copper wiring. Refractory metal binary and ternary nitrides are widely recognized as a class of materials which can be used as diffusion barriers in metal-semiconductor contacts[1]. Among those refractory metal nitrides, zirconium-base and tantalum-base nitride thin films, such as ZrSiN and Ta-Si-N, have been extensively studied as diffusion barriers for copper wiring[2-5]. Although ZrSiN and TaSiN barriers exhibit good performance as diffusion barriers, high resistivity limits their microelectronic applications. HfSiN is a new type of diffusion barrier. This films have high temperature of the crystallization and low charge trap density[6-8]. Herein, different deposition temperature and ratio of N2/Ar were investigated on the effect of the HfSiN film resistivity, and the HfSiN/Cu/HfSiN/SiO2/Si structures were prepared and annealed at temperatures varying from 500 to 600˚C.

Experiment

The specimens were prepared in JPG500A Multi-Function UHV Magneteon Sputtering System. In order to remove organic contaminants and native oxide, substrates of Si were successively cleaned in an ultrasonic bath with diluted HF solution and then rinsed in deionized water before the activation process. The deposition system was executed under a vacuum condition lower than 6×10−4Pa prior to deposition. During the deposition process, the pressure in vacuum chamber was 4 Pa and the sputtering power is 40 W. The substrate bias voltage was varied from 40 to 160 V without substrate heating.

Main target material uses Hf target and silicon target. The purity of target material is 99.99%.HfN and SiN films composed HfSiN .In order to achieve 45nm HfSiN/Cu/HfSiN/SiO2/Si structures,5nm HfSiN films were deposited on the Si substrates by magnetron sputtering, 35nm Copper films covered on the HfSiN films, then 5nm HfSiN films covered on Cu films. Three HfSiN/Cu/HfSiN/SiO2/Si specimens were annealed at 500 °C, 550°C and 600°C for an hour in oxygen ambient, respectively. XRD was used to determine the mass density of the gas-deposited and annealed samples, and it was

operated at 40 kv and 40mA, with Cu-Kα radiation The surface of the barrier samples was characterized by a scanning electron microscopy (SEM), and it was operated at 30 kv.

Results and Discussion

N2/Ar ratio on HfSiN film resistivity

As can be seen from Figure 1， when the proportion of nitrogen increases, HfSiN resistivity increases. When the proportion of nitrogen is lower, more Hf atoms deposited on the Si substrate, forming the thin film of Hf content is high, a relatively low resistivity of the film; with N2 / (N2 + Ar) increase in the proportion, Hf, and N2 to increase the intensity of the reaction on the substrate is formed of a high resistance value compound film.

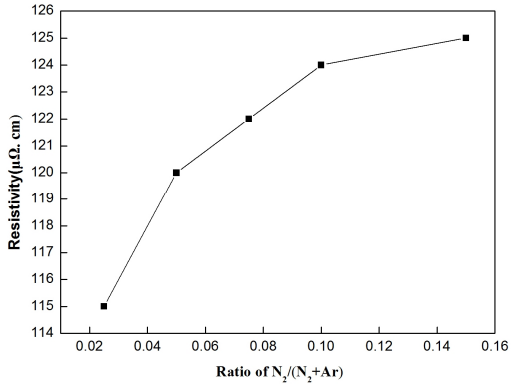

Fig. 1 Electrical resistivity of HfSiN film as a function of nitrogen proportion

Effect of temperature on HfSiN film

Figure 2 is deposited at different temperatures HfSiN film resistivity change. As can be seen from the Figure 2, the resistivity of the film decreases with the increase of the operating temperature . When the temperature was raised to 400 ˚C, resistance of the resulting film was 100μΩ • cm. When the temperature is low, the critical nucleation free energy is small, and the number of core grains formed in the formation of many small, poor crystallinity, greater resistivity.

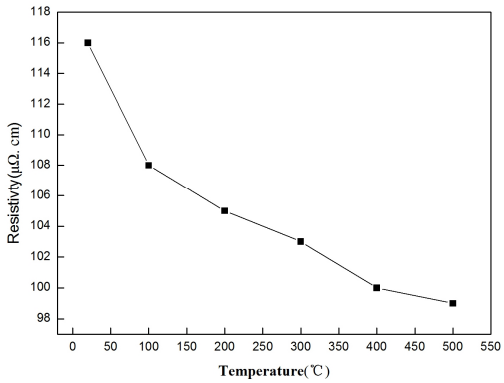

Fig.2 Electrical resistivity of HfSiN film as different temperature

XRD analysis of the multi-layer film before and after annealing

Figure 3(baselayer) is a diffraction pattern of multilayer film (HfSiN/Cu/HfSiN/SiO2/Si) before annealing by XRD. There is only the elemental Hf (111) peaks, which indicates that amorphous Hf has been deposited on the silicon substrate. Figure 3(interlayer) shows that CuO (111) CuO (-111) and HfO2 appear in the multilayer film after being annealed at 550 ˚C.. This peaks explain Cu and Hf start oxidation. When the sample annealed at 600 ˚C in the Figure 3(toplayer), in addition to CuO (111) and CuO (-111) diffraction peak, the sample also appeared Si(111) diffraction peak. After being annealed at 550 ˚C, copper diffusion occurs, HfSiN film of copper diffusion barrier properties of the gradual failure; After annealing at 600 ˚C lot of copper diffusion occurs through HfSiN layer, forming a large amount of CuO, this time HfSiN copper diffusion barrier properties of completely failure.

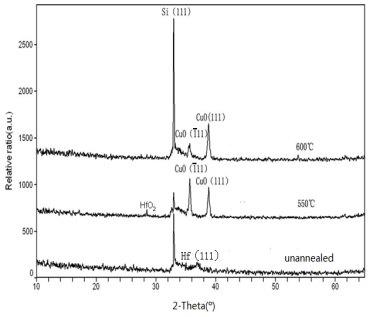

Fig.3 XRD of HfSiN/Cu/HfSiN/SiO2/Si film before and after annealing

SEM images of multilayer films before and after annealing

As can be seen from Figure 4, in the multilayer film without annealing HfSiN/Cu/HfSiN/SiO2/Si smooth surface without generating large particles to exist as amorphous. Under 550 ˚C high temperature annealing to form a small number of large particles. At 600 ˚C generate a large number of large particles, then the following HfSiN thin Cu grain boundary diffusion through the large surface of the O to form a copper oxide, leading to a sharp rise in resistivity, resulting in failure of the barrier layer.

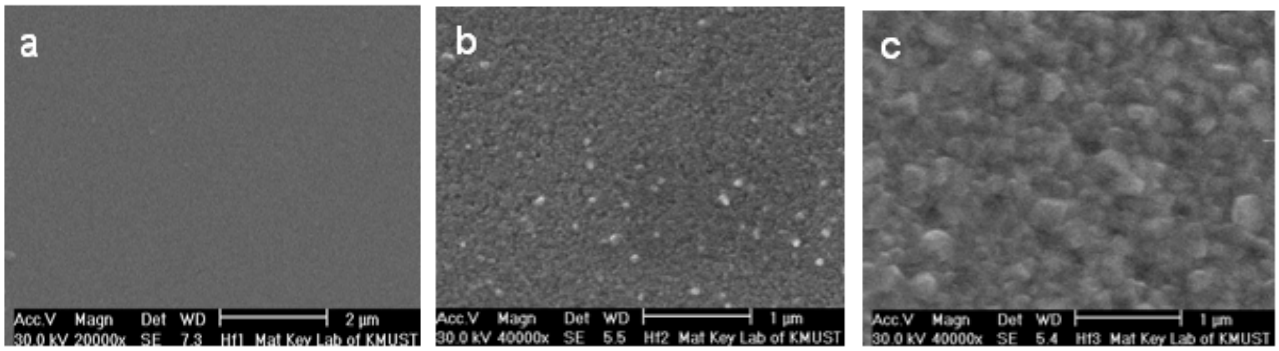

Fig.4 SEM of HfSiN/Cu/HfSiN/SiO_2/Si film before and after annealing

Conclusions

Under different experimental conditions HfSiN parameters and HfSiN / Cu / HfSiN / SiO2/Si multilayer films prepared by magnetron sputtering technique in this article. The effects of temperature, the ratio of nitrogen and argon prepared HfSiN film. Also investigated HfSiN films of Cu diffusion barrier properties under sub-45nm-class process conditions.The results show that the nitrogen content is 2.5% of nitrogen gas and argon gas mixture corresponding HfN film resistivity ratio is less than the resistivity of the other samplesUnder conditions of 550˚C annealing in an oxygen atmosphere can be maintained good HfSiN film copper diffusion barrier properties. When the temperature exceeds 550 ˚C, the resistivity increases sharply multilayers beyond the range, and the formation of CuO material, so that the film HfSiN ability to copper diffusion barrier failure.

Acknowledgements

This work was **s**upported by the technology innovation find of the ministry science and technology in China(No.04C2615200858). This work was financially supported by Guizhou Branch of J word(LKA2013-15).

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