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Nitrogen impurity effects of W–B–C–N quaternary thin film for diffusion barrier for Cu metallization

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Abstract To investigate the thermal stability of nitrogen stuffing effect of tungsten–boron–carbon–nitrogen (W–B–C–N) thin diffusion barrier, the binding energy shift was studied for various annealing temperature. The X-ray diffraction patterns, the deposition rates and the resistivities of W–B–C–N thin film were measured as a function of nitrogen gas ratios for various annealing temperatures and the binding energy between tungsten and nitrogen was determined by the X-ray photoemission spectroscopy. The interface of Cu/W–B–C–N/Si multilayer was characterized for various nitrogen impurity concentration. Our experimental results indicate that W–B–C–N thin films are effective diffusion barriers to prevent the interdiffusion between Cu and Si interface after annealing up to 850 °C for 30 min.

Keywords W–B–C–N thin film · Diffusion barrier · Copper metallization

1 Introduction

Thermally stable metallization technique is one of the most important issues for submicron Si processes. Because miniaturization process causes serious problems such as increasing contact resistance due to silicidation, mechanical failure, adhesive failures, and degradation of shallow junction by interdiffusion of W and Si during heat treatment, and so on [1–3]. Many peoples have studied refractory metal nitrides, such as TaN, ZrN, and WN has been studied to establish a thermally stable tungsten contact system, but these metal-nitride barriers have many problems, such as poor step coverage, residual stress, and poor control of stoichiometry of the metal-nitride composition. Recently, we reported tungsten–boron–carbon–nitrogen (W–B–C–N) thin films are very effective for preventing the silicidation and encroachment. The interaction between Si and Cu is strong and detrimental to the electrical performance of Si even at temperatures below 400 °C. Therefore, it is necessary to implement a barrier layer between Cu and Si. Here, we suggest the tungsten–boron–carbon–nitrogen thin film deposited by rf magnetron sputtering method as a effective diffusion barrier for preventing the Cu diffusion [1,4–6]. From this study, we get the nitrogen impurity effects of W–B–C–N thin films by stuffing effect that was very effective for preventing the interdiffusion between metal and silicon during the subsequent high-temperature annealing process.

2 Experiments

Tungsten boron carbon nitride thin films were deposited on Si substrates by using a magnetron sputtering system. Substrates were *p*-doped (100) oriented Si wafers with resistivities of 5–6 Ω-cm. Prior to sputtering, substrates were cleaned (by using Radio Corporation of America method), spun-dried, and loaded into deposition chamber. Sputtering targets were tungsten with a purity of 99.99%, tungsten boride (W_2B) with a purity of 99.95%, and tungsten carbide (WC) with a purity of 99.95%. Before deposition, Ar pre-sputtering was performed to remove native oxide layer on top of the target. The deposition temperature was maintained at room temperature during the

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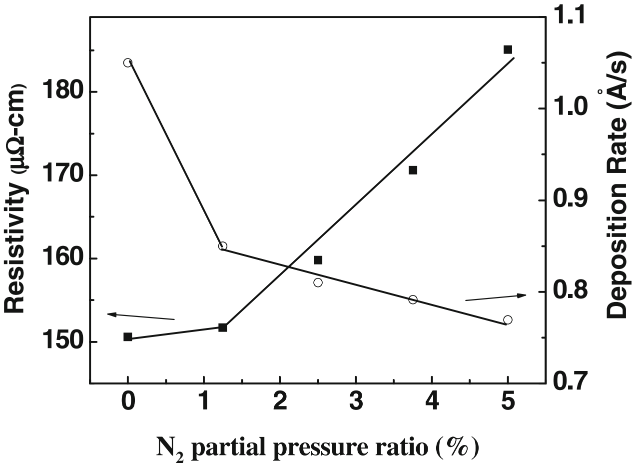


Fig. 1 The resistivity and the deposition rate vs N_2 gas flow rate of W–B–C–N thin films of as-deposited states

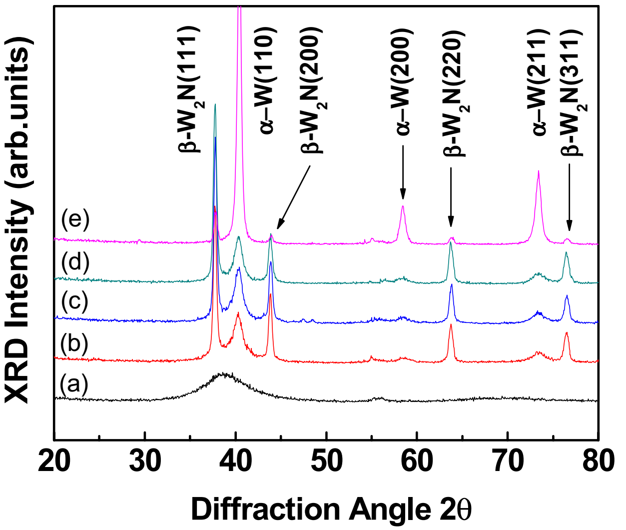


Fig. 3 The XRD patterns of W–B–C–N thin films of (**a**) as-deposited state and of annealed state annealing at (**b**) 700 °C, (**c**) 800 °C, (**d**) 900 °C, and (**e**) 1000 °C for N_2 p.p.r. of 5%

sputtering process. The flow rates of N_2 and Ar gases were separately controlled with mass flow controllers. The total pressure of the sputtering reactor was kept at a constant value of 3 mTorr while the N_2 partial pressure ratio (N_2 p.p.r.) was varied from 0% to 5%. The co-sputtering condition was that the RF power density of the W target was varied from 4 to 7 W/cm^2, that of the W_2B target was varied from 0.7 to 1.4 W/cm^2, and that of the WC target fixed at 0.25 W/cm^2. The thickness of W–B–C–N thin film was varied from 50 to 100 nm.

The deposition rate and the resistivities of as-deposited W–B–C–N thin films were measured by using a α-step, β-ray, and four-point probe, respectively. After thermal treatment at various temperatures for 30 min in a N_2 ambient, the phase transition of the W–B–C–N thin film and the interfacial reaction of the W–B–C–N/Si thin film were investigated by using X-ray diffraction (XRD). X-Ray photoemission spectroscopy (XPS) was used to study the bond structures of W, B, C, and N, as well as the chemical binding energies of each atom. The thermal stability of the W–B–C–N barrier was investigated for various annealing temperatures. Copper was coated on the W–B–C–N/Si substrate by using a thermal evaporator. Annealing process was performed from 700 °C to 900 °C for 30 min in a N_2 ambient. The surface characteristics were studied with nomarski microscope.

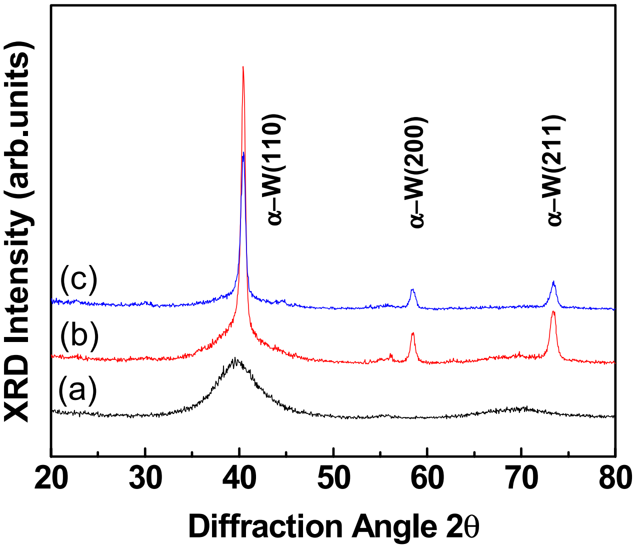


Fig. 2 The XRD patterns of W–B–C thin films of (**a**) as-deposited state and of annealed state annealing at (**b**) 700 °C, and (**c**) 800 °C for N_2 p.p.r. of 0%

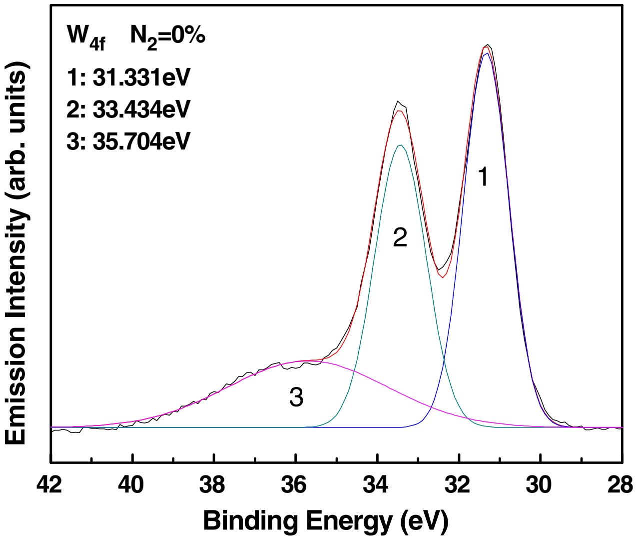


Fig. 4 The XPS spectra of W–B–C thin films with N_2 p.p.r. of 0% after annealing at 700 °C

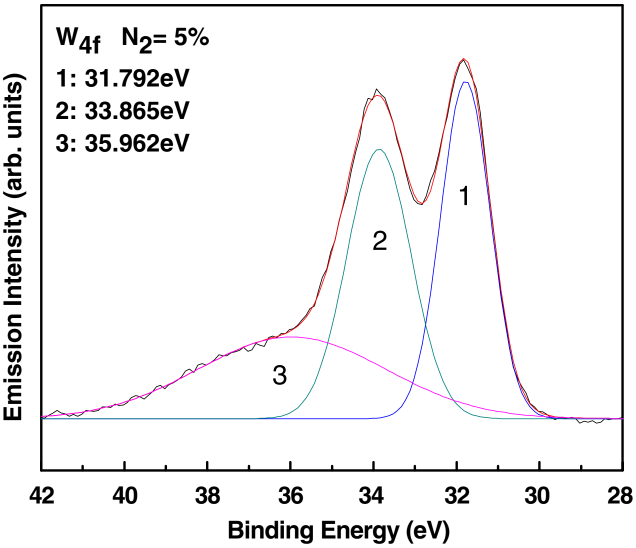


Fig. 5 The XPS measurements of the W–B–C–N thin films with N_2 p.p.r. of 5% after annealing at 700 °C

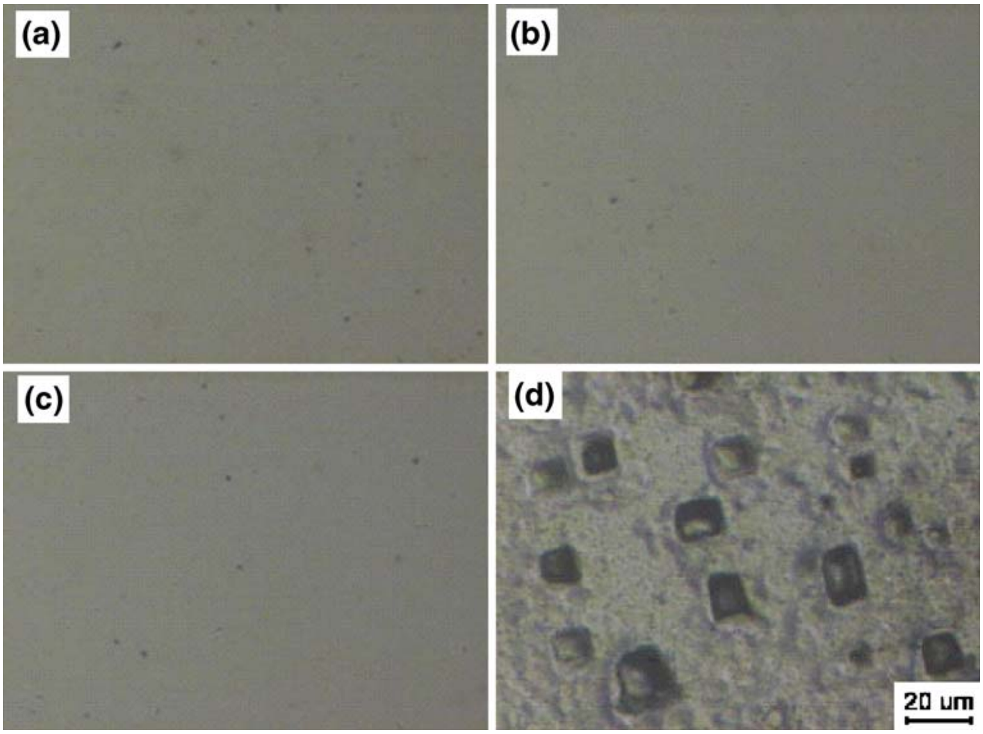
3 Results and discussion

Figure 1 shows the resistivity and the deposition rate as a function of N_2 gas flow rate of W–B–C–N thin films of as-deposited states. The resistivity increased as N_2 p.p.r. was increased from 0% to 5%. Resistivity was a little increased from 150.59 to 151.7 μΩ-cm as N_2 p.p.r. changed from 0% to 1.25%. After then, the resistivity increased linearly from 151.7 to 185.08 μΩ-cm as the N_2 p.p.r. changed from 1.25% to 5%. The deposition rate decreased abruptly from 1.05 to 0.85 Å/s as the N_2 p.p.r. increased from 0% to 1.25%, and then the deposition rate decreased linearly from 0.85 to 0.77 Å/s as the N_2 p.p.r. changed from 1.25% to 5%. Thus, the resistivity increased linearly and the deposition rate decreased linearly as N_2 p.p.r. increases over 1.25%. and these results may be due to the lower Ar gas contents with increasing the N_2 p.p.r. (N_2 p.p.r. increase, Ar+N_2=3 mTorr) which were related to the sputtering yield of W, W_2B and WC target. So resistivity and deposition rate decreased and increased.

Figure 2 shows the XRD patterns of W–B–C thin films for as-deposited state and annealed state annealing up to 800 °C for 30 min with N_2 p.p.r. of 0%. Fig. 2(a) shows that the W–B–C thin film of as-deposited state has amorphous phase while Fig.2(b) and (c) show that the W–B–C thin film of annealed states annealing at 700 °C and 800 °C and the W–B–C thin film have crystallized. The (110), (200), and (211) oriented α-W peaks were observed at 40.51°, 58.53°, and 73.57°, respectively. The role of boron and carbon impurities were not to contribute the crystal structure but to prohibit the inter-diffusion of W and Si.

Figure 3 shows the XRD patterns of W–B–C–N thin films for as-deposited state with N_2 p.p.r. of 5%. Fig. 3(a) shows that the W–B–C–N thin film had amorphous phase while Fig. 3(b–e) show that the W–B–C–N thin film was annealed states annealing up to 1000 °C for N_2 p.p.r. of 5%. The (110), (200), and (211) oriented α-W peaks were

Fig. 6 Nomarski micrographs of Si surface for Cu/W–B–C–N/Si thin film produced by the N_2 p.p.r. of 5% for various annealing temperatures annealing at (**a**) 700 °C, (**b**) 800 °C, (**c**) 850 °C, and (**d**) 900 °C



observed at 40.39°, 58.43°, and 73.35°, along with the (111), (200), (220), and (311) oriented β-W_2N peaks were observed at 37.73°, 43.87°, 63.73°, and 76.62°, respectively. For the W–B–C–N thin films annealed at 1000 °C (Fig. 3(e)), intensity of β-W_2N peaks decreased and intensity of α-W peaks increased. It is due to expel the nitrogen from inside the W–B–C–N thin films annealed over than 900 °C. From these results (Figs. 2 and 3), the role of nitrogen impurities in W–B–C–N thin films was stuffing effect that the W–B–C–N thin film was very effective for preventing the interdiffusion between metal and silicon during the subsequent high-temperature annealing process (900 °C).

In order to study the impurity behaviors of the W–B–C–N thin films after annealing at 700 °C for 30 min with N_2 p.p.r. of 0% and 5%, the binding energy was measured with XPS as shown in Figs. 4 and 5. The relative X-ray photoemission intensities of the doublet peaks of W_{4f} of W–B–C–N thin film were given by the ratio of their respective degeneracies (2j+1). The doublet peaks of W_{4f} 7/2 and 5/2 states were 31.33 and 33.43 eV for N_2 p.p.r. of 0% after annealing at 700 °C (Fig. 4), and that of W_{4f} 7/2 and 5/2 states are 31.79 and 33.87 eV for N_2 p.p.r. of 5% (Fig. 5) after being annealed at 700 °C. The doublet peaks of W_{4f} (7/2 and 5/2 states) were shifted by 0.46 and 0.43 eV. The binding energy shift between the N_2 p.p.r. of 0% and 5% was caused by the extraction of nitrogen that the nitrogen was expelled from the bulk to the surface in the W–B–C–N thin film so quickly for N_2 p.p.r. of 0% rather then 5%. From these results, the binding energy shift of W–B–C–N thin film after annealing at 700 °C was due to the expelling of nitrogen from the bulk to the surface inside the W–B–C–N thin film.

Hence, we also investigated the role of an interface layer, such as a W–B–C–N layer, between Cu metal and Si substrate. The procedures were as follows: Cu/W–B–C–N/Si thin films were annealed at various annealing temperatures. After that, Cu and W–B–C–N thin film were preferentially etched with a Wright etchant, which was useful for observation of defects generated by the interdiffusion of Cu and Si. Figure 6 shows the Nomarski micrographs of Si surface after the Cu/W–B–C–N thin film had been annealed from 700 °C to 900 °C for 30 min and etched. In the W–B–C–N thin film deposited at a N_2 p.p.r. of 5%, neither Cu-decorated microdefects nor dislocations appeared after annealing even at 850 °C. However, Cu-decorated defects were observed after annealing at 900 °C. Cu atoms penetrated through W–B–C–N diffusion barrier, and Cu atoms diffused into the Si substrate along (110) direction that had generated many dislocations.

4 Conclusion

Tungsten–boron–carbon–nitride diffusion barrier were studied with Cu/W–B–C–N/Si structure. Impurities, such as nitrogen in the 1,000 Å-thick W–B–C–N thin films, provided a stuffing effect that was very effective for preventing the interdiffusion between the metal and the silicon during the subsequent high-temperature annealing process. The resistivity increased linearly and the deposition rate decreased as N_2 p.p.r. increased over 1.25%. Changes in XRD peaks and XPS curves were observed due to the nitrogen being expelled from the bulk to the surface inside of the W–B–C–N thin film. From Nomarski micrographs of the Si surface, neither Cu-decorated microdefects nor dislocations appeared after annealing, not even at 850 °C. After annealing at 900 °C, Cu atoms had penetrated through the W–B–C–N diffusion barrier, and it had diffused into the Si substrate along (110) direction that had generated many dislocations.

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