

# Investigation of cosputtered W-C thin films as diffusion barriers

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Polycrystalline thin films of W-C were deposited on single-crystal  $\langle 111 \rangle$ Si or  $\text{SiO}_2$  substrates by rf planar magnetron cosputtering of graphite (C) and W targets. The performance of cosputtered  $\text{W}_{75}\text{C}_{25}$  thin films as diffusion barriers between a  $\langle 111 \rangle$ Si substrate and metallic overlayers of Ag, Au, or Al was investigated. Backscattering spectrometry and x-ray diffraction are used to detect metallurgical interactions. Four-point probe measurement of resistance is employed to monitor the electrical stability of the metallization schemes upon thermal annealing in a vacuum for 30 min in temperature ranges from 500 to 700 °C. The electrical resistivity of  $\text{W}_{75}\text{C}_{25}$  films is  $140\ \mu\Omega\ \text{cm}$ . A  $\text{W}_{75}\text{C}_{25}$  layer 1100 Å thick prevents metallurgical interdiffusion and reaction between Au or Ag overlayers and the  $\langle 111 \rangle$ Si substrates up to 700 °C, and between an Al overlayer and the  $\langle 111 \rangle$ Si substrate up to 450 °C.

## I. INTRODUCTION

An ideal thin-film diffusion barrier for a contact metallization scheme is a layer of materials which has these capabilities: high-temperature stability, chemical stability, and good electrical conductivities to inhibit interdiffusion between its bordering media.<sup>1-3</sup> The borides, carbides, and nitrides of refractory metals are such materials and therefore attract attention for thin-film diffusion barriers. Refractory metal nitrides, such as  $\text{TiN}$ ,<sup>4-6</sup>  $\text{TaN}$ ,<sup>7</sup>  $\text{WN}$ ,<sup>8</sup> and  $\text{HfN}$ ,<sup>9</sup> have been studied by many researchers. A typical research method is to reactively sputter deposit the refractory metal nitrides on a silicon substrate, and then cover it with an overlayer of a metal such as Al, Ag, and Au. Diffusion barriers of refractory metal diborides have also received research attention.<sup>10-12</sup> But very few researchers have worked on refractory metal carbides, only TaC (Ref. 13) and TiC (Refs. 13-16) have been studied and reports published so far.

This study was primarily to investigate the properties of tungsten carbide as a diffusion barrier. In order to select a suitable tungsten carbide film for our investigation, preliminary experiments are conducted to observe and compare the properties of carbide films with different compositions ( $\text{W}_{75}\text{C}_{25}$  and  $\text{W}_{43}\text{C}_{57}$ ). The results showed that cosputtered  $\text{W}_{75}\text{C}_{25}$  films possess better electrical and thermal stability than  $\text{W}_{43}\text{C}_{57}$  films. The subsequent experiments of diffusion barriers have therefore been carried out only with the  $\text{W}_{75}\text{C}_{25}$  films.

The  $\text{W}_{75}\text{C}_{25}$  films as diffusion barriers were examined between metallic overlayers of Al, Ag or Au, and Si or  $\text{SiO}_2$  substrates in multilayer metallization schemes. The results show that metallurgically, all these schemes have good thermal stability especially for Ag metallization.

## II. EXPERIMENTAL PROCEDURES

The thin films of W-C were deposited by cosputtering W and graphite C targets on  $\langle 111 \rangle$ -oriented 0.001-0.005  $\Omega\ \text{cm}$  silicon substrates and  $\text{SiO}_2$  substrates at room temperature.

The Si and  $\text{SiO}_2$  (thermal oxidized Si) substrates were cleaned by an ultrasonic agitator in consecutive baths of or-

ganic solvents (trichloroethylene, acetone, and methanol), followed by cleaning in a 10% HF solution and rinsing in high-purity deionized water prior to loading into the sputtering chamber. The rf planar magnetron sputtering system used was equipped with a conventional oil diffusion pump and cold trapped with liquid nitrogen. The sputtering chamber background pressure was  $2 \times 10^{-7}$  Torr. A 3-in. graphite C target partially covered with W strips was used as a cosputtering source. The C and W concentrations were varied by changing the number of W strips. Sputtering was conducted with pure Ar at 6-mTorr pressure, 250-W rf power, and a -5-V dc bias at the substrate. No external heating or cooling of the substrate holder was used. The substrate was kept stationary under the target. The resulting deposition rate for the W-rich films was 200 Å/min, and 150 Å/min for the film of near-equal composition. The metallic overlayers were deposited by rf sputtering, without breaking vacuum, using elemental targets contained in the same system and pure Ar as the sputtering gas.

Finally, for the heat treatment, the samples were placed in a vacuum furnace at pressure below  $3 \times 10^{-7}$  Torr and annealed at a temperature range from 400 to 800 °C for 30 min.

Backscattering spectrometry (BS) of 2-MeV  $^4\text{He}^+$  was used to monitor the films before and after thermal treatment. The phase and structure of the reaction products were identified by glancing angle x-ray diffraction (Read Camera). The compositions were measured by BS. The electrical conductance in the overlayer(s) on Si or  $\text{SiO}_2$  substrates before and after annealing was determined by four-point probe measurements at room temperature. The surface morphologies were observed by scanning electron microscopy (SEM).

## III. RESULTS AND DISCUSSIONS

### A. Composition and characterization of W-C films on $\text{SiO}_2$ substrates

From BS data of the cosputtered W-C thin films deposited onto carbon substrates, the average composition of the films is  $\text{W}_{75}\text{C}_{25}$  and  $\text{W}_{43}\text{C}_{57}$  with an estimated error of  $\pm 5\%$ .

Both types of as-deposited thin films are polycrystalline in structure, as established by x-ray diffraction. The phase of both film types of SiO<sub>2</sub> substrates was identified by glancing angle x-ray diffraction after each heat treatment. No phase change was observed for heat annealing of 30 min at up to 800 °C. Films with composition W<sub>43</sub>C<sub>57</sub> are of the cubic WC<sub>1-x</sub> phase and have a room-temperature resistivity of 100 μΩ cm. Films with composition W<sub>75</sub>C<sub>25</sub> are of the hexagonal α-W<sub>2</sub>C phase and have a room-temperature resistivity of 140 μΩ cm. Upon annealing, the ratios of the sheet resistance are almost constant over the whole temperature range (<800 °C) investigated. They suggest that both films are stable and do not undergo chemical changes or interfacial reaction with the oxidized Si substrates. BS spectra confirm that the W<sub>75</sub>C<sub>25</sub> and W<sub>43</sub>C<sub>57</sub> films demonstrate no detectable metallurgical reaction with the oxidized Si substrates. The spectra yielded thicknesses of 110 nm for W<sub>75</sub>C<sub>25</sub> and 150 nm for W<sub>43</sub>C<sub>57</sub>, from which both resistivities of 140 and 100 μΩ cm are deduced. The SEM micrographs also show that the surface morphology of both annealed samples remain flat and no pits are formed.

## B. Interaction between polycrystalline W-C films and Si substrates

No interdiffusion and interfacial reaction between W<sub>75</sub>C<sub>25</sub> (or W<sub>43</sub>C<sub>57</sub>) films and Si substrates are detectable up to 800 °C for 30 min by 2 MeV <sup>4</sup>He BS spectrometry. After a 900 °C annealing, a little interfacial reaction was noted.

The sheet resistance of W<sub>75</sub>C<sub>25</sub> films on a Si substrate remains unchanged up to 700 °C annealing, and then decreases only slightly after 800 °C annealing. This indicates that neither metallurgical nor chemical reactions occur between barrier layers of W<sub>75</sub>C<sub>25</sub> and Si substrates below 700 °C. From SEM pictures, the surface of the samples are flat and no changes are observed.

For W<sub>43</sub>C<sub>57</sub> films on Si substrates, the SEM micrographs reveal that some blisterlike defects (see Fig. 1) develop in the film at 700 °C. The morphology of the defects suggests a localized loss of adhesion at the interface. The number of these blisters is few and does not alter the sheet resistance. At

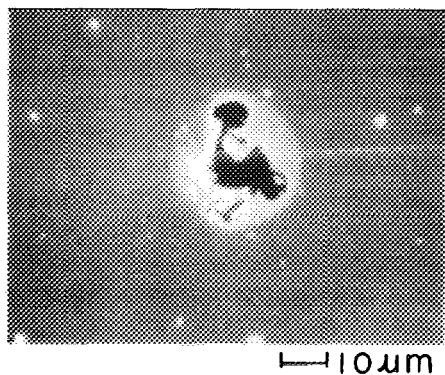


FIG. 1. SEM micrographs of a W<sub>43</sub>C<sub>57</sub>/Si(111) sample annealed at 700 °C for 30 min.

800 °C, however, the number of blisters increases which raises the sheet resistance.

The above experimental results indicate that thin films of the composition W<sub>75</sub>C<sub>25</sub> have better thermal and chemical stability than W<sub>43</sub>C<sub>57</sub> films. One possible reason is the difference of strain in the films, either intrinsic or extrinsic. Therefore, the W-rich films were chosen as diffusion barriers for our later investigation.

## C. W<sub>75</sub>C<sub>25</sub> thin films as diffusion barriers

### 1. Al/W<sub>75</sub>C<sub>25</sub>/Si(111) system

A cosputtered W<sub>75</sub>C<sub>25</sub> film (~1100 Å) and a Al film (~700 Å) were consecutively deposited onto a Si substrate. The configuration of the sample is shown in the insert of Fig. 2. The BS spectra of Fig. 2 show that interdiffusion between Al and W<sub>75</sub>C<sub>25</sub> films occurs at 500 °C. The lowering and broadening in the Al signal and the formation of a high-energy step in the W signal indicate that Al and W form a surface layer of fairly uniform composition. X-ray diffraction from these samples identifies the presence of the intermetallic compounds of WAl<sub>12</sub> and Al<sub>4</sub>C<sub>3</sub>.

Figure 3 shows sheet resistance ratio versus annealing temperature for this system. Up to 450 °C, the ratio remains fixed and then rises at the same time as the reaction between Al and W<sub>75</sub>C<sub>25</sub> proceeds. These results all indicate that a significant metallurgical interreaction occurs at above 450 °C between the Al and the W<sub>75</sub>C<sub>25</sub> layers. SEM micrographs show that the surface morphology of the samples remains flat and no pits are formed.

It is well known that the nitrides of refractory metals, such as TiN (Refs. 4-6) and WN,<sup>7</sup> are quite stable. In an attempt to improve the stability of polycrystalline W<sub>75</sub>C<sub>25</sub> film as a diffusion barrier, nitrogen has been introduced into the W<sub>75</sub>C<sub>25</sub> film during sputtering deposition by using a mixture of 90% Ar and 10% N<sub>2</sub> gases. The following experimental results were obtained. The amorphous structure of W-C-N film was observed by x-ray diffraction pattern before and after thermal annealing. The sheet resistance of the W-C-N

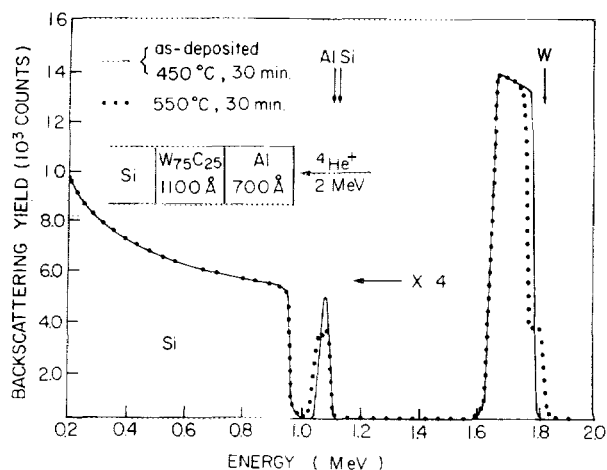


FIG. 2. 2-MeV <sup>4</sup>He<sup>+</sup> backscattering spectra of polycrystalline W<sub>75</sub>C<sub>25</sub> films in the configuration Al/W<sub>75</sub>C<sub>25</sub>/Si(111), as deposited (solid line) and annealed at 550 °C (filled dots) for 30 min.

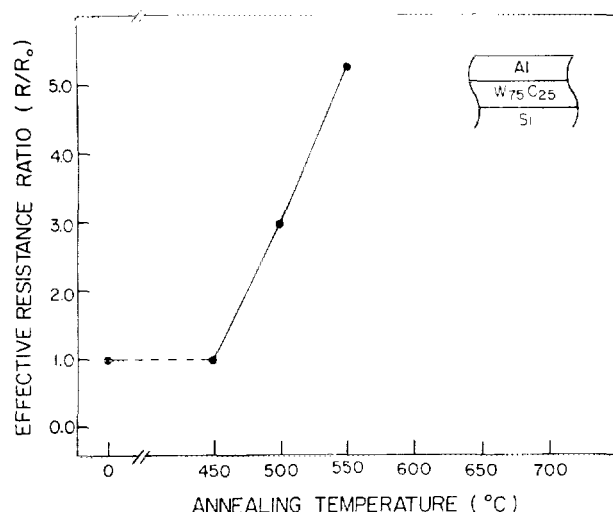


FIG. 3. Normalized sheet resistance of the configuration of Al/W<sub>75</sub>C<sub>25</sub>/Si(111), after ( $R$ ) and before ( $R_0$ ) vacuum annealing for 30 min as a function of annealing temperature.

film was  $\sim 250 \mu\Omega \text{ cm}$ . The BS data indicated that the W-C-N film was stable at least up to 500 °C as a diffusion barrier between the Al overlayer and Si substrates. A significant metallurgical interaction was detected at 600 °C annealing. The W-C-N film was more stable than the W<sub>75</sub>C<sub>25</sub> film. This is probably due to the amorphous structure of the W-C-N film which prevents it from grain boundary diffusion. SEM micrographs demonstrate that the samples have blisterlike characters formed on their surface morphology at 600 °C annealing. One possible explanation for this formation is the high intrinsic strain of W-C-N film which induces localized loss of adhesion and delamination in the interface between the barriers and substrates by thermal mismatch. Another possibility is that a local reaction occurs between the Si substrate and the metal overlayer or the diffusion barrier film. The fraction of reacted area may be too small to be detected by x-ray diffraction and BS analysis.

Van Gorp *et al.*<sup>17,18</sup> reported that annealing of the Al/W/silicide systems did not show any reaction products at annealing temperature below 500 °C. Annealing for 30 min at 500 °C showed the formation of cubic WAl<sub>12</sub> between Al and W layers and no reaction products between Al and silicide. From our experimental results and theirs, we believed that the failure mechanism of the thin-film barrier layer of W<sub>75</sub>C<sub>25</sub> is grain boundary diffusion of Al into the polycrystalline W<sub>75</sub>C<sub>25</sub> layer. It then reacts with the barrier layer to form compounds WAl<sub>12</sub> and Al<sub>4</sub>C<sub>3</sub> near 500 °C. The effective resistance increase is mainly due to the bonding of aluminum in the top layer.

## 2. Au/W<sub>75</sub>C<sub>25</sub>/Si(111) and SiO<sub>2</sub> systems

The metallurgical interaction between a cosputtered W<sub>75</sub>C<sub>25</sub> layer ( $\sim 1100 \text{ \AA}$ ) and a Au film ( $\sim 3000 \text{ \AA}$ ) were studied on Au/W<sub>75</sub>C<sub>25</sub> bilayers deposited onto Si and SiO<sub>2</sub> substrates. The BS spectra of samples of Au/W<sub>75</sub>C<sub>25</sub>/Si(111) show no detectable metallurgical reaction before and after annealing at 700 °C for 30 min.

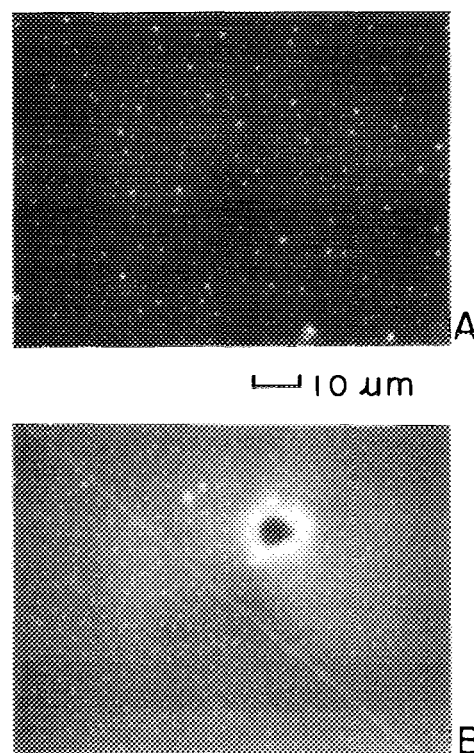


FIG. 4 (a) and (b) SEM micrograph of the Au/W<sub>75</sub>C<sub>25</sub>/Si(111) samples annealed at 700 °C for 30 min.

In both Au/W<sub>75</sub>C<sub>25</sub>/Si(111) and SiO<sub>2</sub> systems, below 500 °C annealing, the ratio of sheet resistance was reduced  $\sim 40\%$ . The decrease of resistivity is probably due to the grain growth of thin films and the reduction of defects after annealing which decreases the electron scattering. In annealing temperature between 500 and 700 °C, the ratio of sheet resistance remained the same, and no detectable interfacial reaction was shown to occur between the overlayer of Au and the barrier layer of W<sub>75</sub>C<sub>25</sub>. From SEM micrograph, it can be seen that blisters about 1- $\mu\text{m}$  diameter formed on the entire surface of Au [Fig. 4(a)] and also a number of pits formed on some local regions [Fig. 4(b)] after 700 °C annealing for 30 min. This may be attributed to thermal mismatch or local reaction as described above.

## 3. Ag/W<sub>75</sub>C<sub>25</sub>/Si(111) and SiO<sub>2</sub> systems

When the Au overlayer is replaced by a Ag layer ( $\sim 2000 \text{ \AA}$ ), virtually no metallurgical reaction was detected even at 700 °C for 30 min by 2-MeV <sup>4</sup>He BS spectra (see Fig. 5). A little change was observed between the rear edge of Ag and the front edge of W (from W<sub>75</sub>C<sub>25</sub>) in the BS spectra after 450 °C annealing for 30 min, but no further change was found until 700 °C, 30-min annealing. This change may be a consequence of the rearrangement of interface between the Ag and W<sub>75</sub>C<sub>25</sub> and change of the grain size of the Ag and W<sub>75</sub>C<sub>25</sub>.

In two configurations of Ag/W<sub>75</sub>C<sub>25</sub>/Si(111) or SiO<sub>2</sub> systems, the annealing below 500 °C, the ratio of sheet resistance was reduced  $\sim 40\%$ . This reduction may be accounted for from the previous discussion of cases of Au/W<sub>75</sub>C<sub>25</sub>/

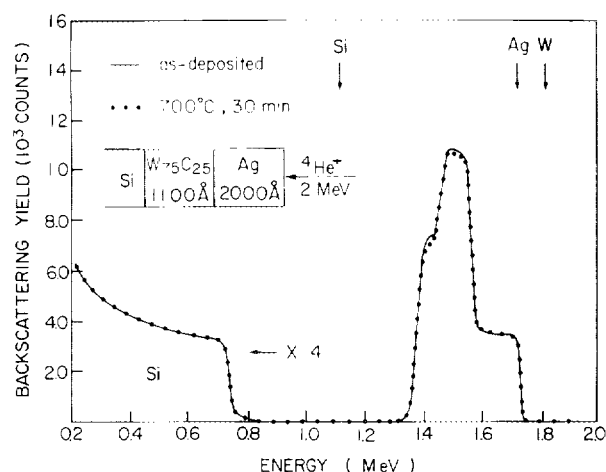


FIG. 5. 2-MeV  $^4\text{He}^+$  backscattering spectra of polycrystalline  $\text{W}_{75}\text{C}_{25}$  films in the configuration  $\text{Ag}/\text{W}_{75}\text{C}_{25}/\text{Si}\langle 111 \rangle$ , as deposited (solid line) and annealed at  $700^\circ\text{C}$  (filled dots) for 30 min.

$\text{Si}\langle 111 \rangle$  or  $\text{SiO}_2$ . For the annealing between  $500$  and  $700^\circ\text{C}$ , the ratio of sheet resistance remained the same which implies that the system is very stable and does not undergo any chemical interfacial reaction between the overlayer of Ag and the barrier layer of  $\text{W}_{75}\text{C}_{25}$ . SEM micrographs show that the surface morphology of the samples is very flat with no blisters observed after  $700^\circ\text{C}$  annealing. It is suggested that the Si-Ag system has a much higher eutectic temperature ( $830^\circ\text{C}$ ) compared to Si-Al ( $577^\circ\text{C}$ ) and Si-Au ( $370^\circ\text{C}$ ) and also no mutual solubility; both may inhibit a metallurgical reaction.

#### IV. SUMMARY AND CONCLUSION

The compositions of thin films of  $\text{W}_{75}\text{C}_{25}$  and  $\text{W}_{43}\text{C}_{57}$  are identified, respectively, as  $\alpha\text{-W}_2\text{C}$  and  $\text{WC}_{1-x}$  structures by x-ray diffraction data. The experimentation has revealed two strengths of the  $\text{W}_{75}\text{C}_{25}$  film as a diffusion barrier. First, it is of high thermal stability remaining stable at temperatures up to  $700^\circ\text{C}$  on Si substrates and  $800^\circ\text{C}$  on  $\text{SiO}_2$  substrates. Second, it is of high electrical stability having sheet resistance  $140\mu\Omega\text{ cm}$ . Therefore, the thin film of  $\text{W}_{75}\text{C}_{25}$  is a

very good candidate for diffusion barrier materials application.

The cosputtered refractory metal carbide  $\text{W}_{75}\text{C}_{25}$  polycrystalline of thin film was studied for application as diffusion barriers between Si substrates and overlayers of Ag, Au, and Al in multiple-layer metallization schemes. It is found that a barrier layer of  $\text{W}_{75}\text{C}_{25}$  prevents the interdiffusion and interaction between Au or Ag overlayers and Si substrate up to  $700^\circ\text{C}$ , and between Al overlayer and Si substrate up to  $450^\circ\text{C}$ , respectively, after the vacuum furnace annealing for 30 min. In the latter case, a possible explanation of the failure mechanism of the barrier layer of  $\text{W}_{75}\text{C}_{25}$  might be the diffusion of Al into the film of  $\text{W}_{75}\text{C}_{25}$  along grain boundaries and the subsequent interaction it has with W and C to form  $\text{WAl}_{12}$  and  $\text{Al}_4\text{C}_3$ .

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