Asian Journal of Information Technology 6 (4): 506-510, 2007
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Study of Tungsten Silicide Composition and Impurities by AES, XPS and SIMS

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Abstract: The composition and impurity concentration within thin films is strongly dependent on the deposition technique used in their preparation. In the present study we have prepared Tungsten silicide thin films by rf cathodic sputtering of a composite target $WSi_{2.7}$ and studied the surface and composition of these samples using Auger Electron Spectrometry (AES) and X-ray Phototoelectron Spectrometry (XPS), the spectra show that the surfaces of the annealed thin films are covered by a thin layer of silicon dioxyde (SiO_2), while the depth profile investigation gives evidence that oxygen is present at the silicide-substrate interface. We also measured the impurity profiles of our thin films using Secondary Ion Mass Spectrometry (SIMS), which is a more sensitive probe and found the following impurities, potassium, chlorine, fluorine, sodium, hydrogen. These impurities originate from the sputtering chamber and the sputtered target.

Key words: AES, XPS , SIMS , impurities, tungsten silicide

INTRODUCTION

Tungsten silicide is widely used as gate electrode and interconnect material in MOS VLSI (very large scale integration) technology, because it provides improved device performance in terms of RC time delay and power consumption (Liang and Chao, 2001). Tungsten disilicide and more generally refractory metal silicides such as $TiSi_2$, $MoSi_2$ and $TaSi_2$ are characterized by their low resistivity and good stability at high temperatures.

These refractory silicide thin films can be obtained by refractory metal deposition on Si (Lee *et al*., 2000) alternate sputtering of the refractory metal and Si (Backhouse *et al*., 1997) sputtering from a composite target made of a refractory metal and Si (Brors *et al*., 1983) co-sputtering a refractory metal and Si (Lee and Suh, 1999) co-evaporation of a refractory metal and Si (Crowder and Zirinsky, 1979) and Chemical Vapor Deposition (CVD) (Bain *et al*., 2002).

During the deposition process various impurities, resulting from the deposition chamber and the materials used in the process, get trapped within the thin films. These impurities may affect quality the annealed thin film and are a source of their high resistivity (Togei, 1986). To control some of the properties such as the electrical resistance and adhesion, accurate knoweledge the film composition is needed. Film composition is generally obtained by Rutherford Back-Scattering Spectrometry (RBS). However, this technique does not provide detailed information on the surface or the interface between the film and its substrate contrary to XPS and AES. Furthermore, it worth noting that in addition XPS also yields information on the chemical environment of atoms near the surface. In this research, using XPS and AES we present our studies of the tungsten silicide thin films composition. We also provide the results of the depth profile measurements for W, Si and O. In as much as impurities are concerned, only qualitative results are obtained from SIMS measurements.

MATERIALS AND METHODS

We deposited tungsten silicide thin fims by rf cathodic sputtering of the composite target $WSi_{2.7}$. Since this deposition technique gives tungsten rich thin films in comparison with the sputtered composite target (Murakami and Shingyoji, 1990) we used a target made of tungten silicide with ratio Si:W = 2.7. This should allow for obtaining thin films whose stoichiometry is close to that of tungsten disilicide WSi_2. The deposition process was carried out in an atmosphere of argon where the sputtering chamber pressure is kept around 10^{-3} mTorr. The films were deposited on a monocristalline Si(110) substrate and the annealing of the resulting films was performed in a furnace with flowing nitrogen, at 1000°C for 30 min. To acquire the AES depth profiles, removal of the surface films was performed by bombardment with an Ar ions beam. The beam scanned surface in this case is a 2×2 mm area which roughly corresponds to an erosion rate of 60Å min^{-1}.

In our AES probing, the energy of the incident electrons is 5KeV and the primary current of electrons is 1 μA. The beam diameter at the probed film is about 200 μm. The SIMS analysis was done in both static and

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dynamic modes where the energy of the incident ions Ar^+ is 5 KeV with an argon pressure of approximately 2×10^{-6}mbar. This corresponds to a current density of 7×10^{-8}A cm^{-2}. In static mode, the erosion rate is very low and one can consider that the state of the surface remains unchanged after a SIMS probing. SIMS profiling were acquired in the dynamic mode where the erosion rate is much more important but remains relatively small. To avoid the crater edge effects (Hoffman, 1976) we only analyse 30% of the scanned surface. These two techniques, AES and SIMS, were combined in a single apparatus identified as LH10 (Leybold Hereaus).

Our XPS analysis was performed using a Mg Ká X-ray as a primary excitation, furthermore the area removed by ionic erosion is 10×10 mm wide because the probed area must be larger than in AES since the probing beam is wider.

RESULTS AND DISCUSSION

AES analysis: The analysis of the deposited thin films showed that they are covered by a thin SiO_2 layer of thickness of about 50 Å. In particular, we observe the Si characteristic peak at 94 eV (Si in SiO_2), but no tungsten peak was found as shown in Fig. 1. It has been shown previously as a tungsten silicide is annealed a silicon oxide forms on its surface (Krusin and Joshi, 1987). After cleaning the thin film surface by ionic erosion for a few minutes to remove the oxide, Si(*LVV*) peak at 92 eV, Si(*KLL*) at 1738 eV and W(*MNN*) peak at 1758 eV appear while, oxygen O(LMM) and carbon C(*KLL*) peaks get weaker in intensity, as indicated in Fig. 2. No appreciable chemical shift was noticed and no information can be drawn on the existing Si-W bonds. Let us also note the presence of the argon peak (*LMM*) at 222 eV. One might first think that this observed argon peak comes from the implantation of impinging atoms near the sample surface during the ionic erosion process. However an RBS study showed that the argon was present in thin films prepared in the same conditions (Karmed and Khellaf, 2006). One can conclude that the origin of this argon is the sputtering chamber itself.

The determination of the films composition was accomplished through the comparison of the heights peak-to-peak heights of Si and W obtained from the composite target WSi_2 and the deposited films.The Si:W ratio was found to be 1.3 in as-deposited films probed where it can be seen that they are are W rich.

Figure 3 shows the Si, W and O depth profile in these films. Among the impurities, we only took the oxygen O(1*s*) peak because its intensity is the only one high enough to be measured. Oxygen is present at the substrate-silicide interface of as-deposited films but after

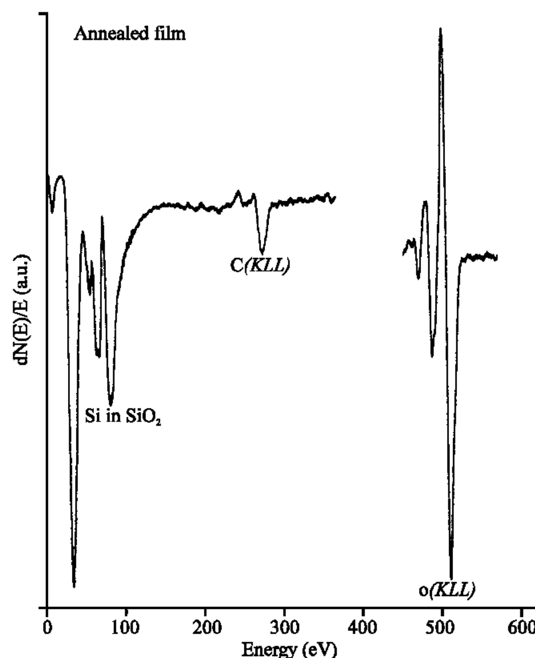

Fig. 1: Full Auger spectrum of annealed WSi_x

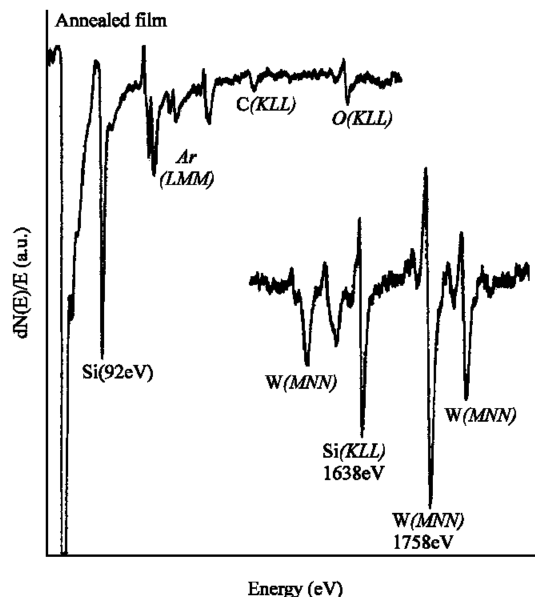

Fig. 2: Full Auger spectrum of annealed WSi_x after a surface cleaning with ionic erosion showing apparition of Si and W peaks

annealing, this peak intensity becomes very weak as shown in Fig. 4 with an increase of the concentration ratio Si:W to 1.8. Obviously, the layer of the native oxide which exists on the Si substrate surface does not constitute a diffusion barrier that prevents diffusion of Si from the substrate toward the WSi_x films in this annealing operation.

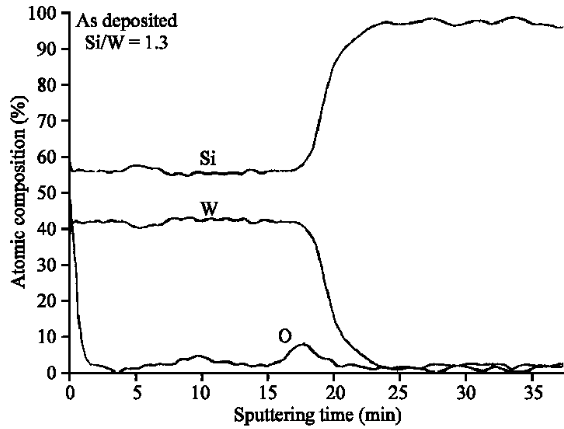

Fig. 3: AES depth profile of as-deposited WSi_x film

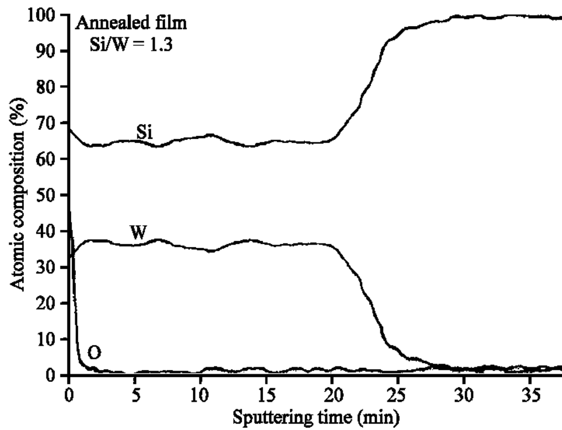

Fig. 4: AES depth profile of WSi_x annealed film

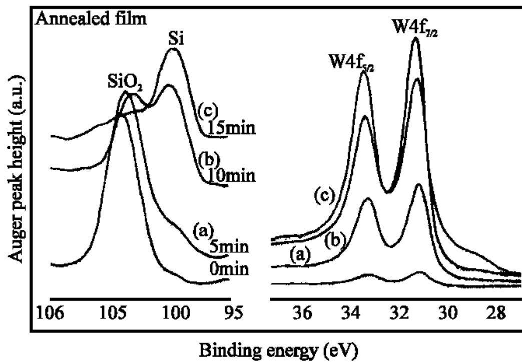

Fig. 5: Si*2p* and W*4f* XPS spectra of WSi_x annealed film after 5a, 10b and 15c min sputtering time

XPS analysis: The results of the films surface analysis by XPS are in agreement with those provided by AES analysis. Indeed, the Si_{2p} peak at 103.6 eV is attributed to Si in SiO_2 as shown in Fig. 5. In fact, after removing this

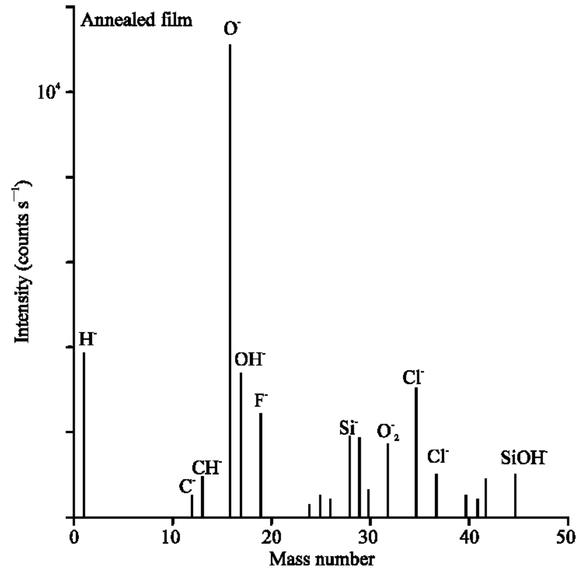

Fig. 6: Negative SIMS spectra of annealed tungsten silicide film

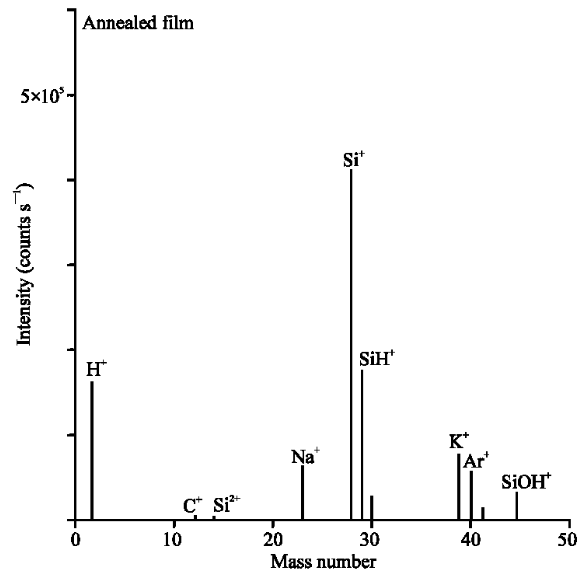

Fig. 7: Positive SIMS spectra of annealed tungsten silicide film

SiO_2 layer, the 103.6 eV peak disappeared completely and we observed new peaks among which the following ones: Si_{2p} and the doublet $W4f_{7/2}$ at and $W4f_{5/2}$, respectively at binding energies 99.2eV, 31.5 eV and 33.6eV. For the W*4f* peaks, it is not possible to say if these peaks are due to metallic tungsten or to tungsten silicides. The Si_{2p} peak at 99.2eV can be attributed either to Si-Si or Si-W bond.

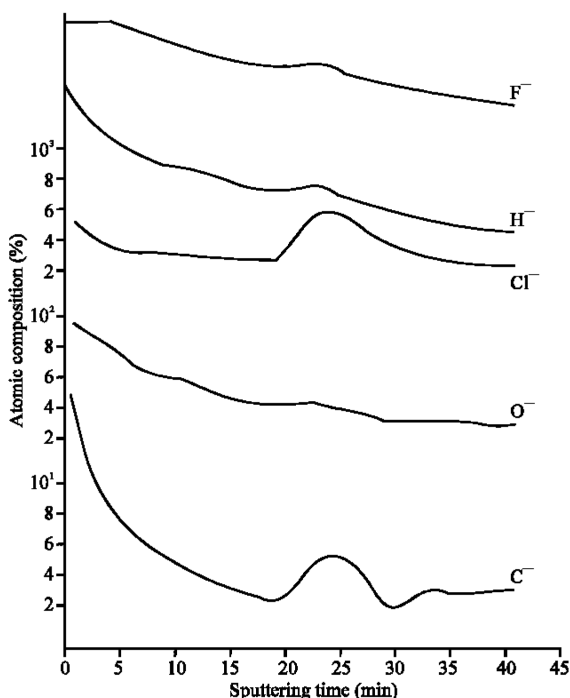

Fig. 8: SIMS depth profiles of some elements after annealing

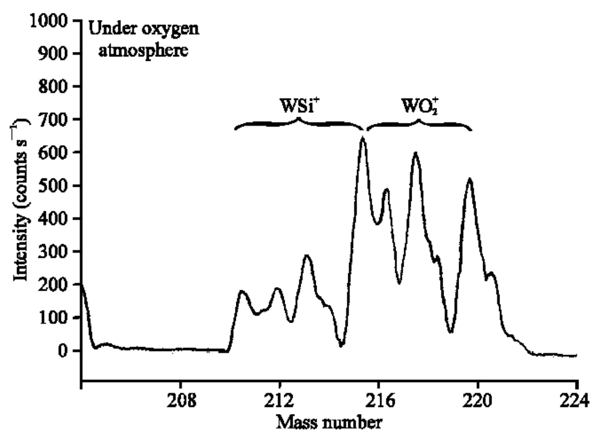

Fig. 9: SIMS spectra obtained by sputtering an annealed film under an oxygen atmosphere

We have calculated the relative atomic concentrations of W and of Si in these films using ORIGIN 7.5 package. Concentrations were evaluated from peak areas after Shirley background subtraction method (Shirley, 1972) using theoretical cross sections and Gaussian curve fitting and the cross sections of Si and W taken from the published literature (Scofield, 1976). We found that the Si:W concentration ratio was around 1.7 for the annealed thin films.

We have to note that ionic erosion leads to a change in the surface composition because the sputtering yields of silicon and tungsten are very different (Hoffman, 1976) and this surface becomes enriched by tungsten.This is a major drawback in determining the concentration of constituents using XPS or AES techniques.

SIMS analyse: We show respectively in Fig. 6 and 7 the spectra obtained, after cleaning the thin films surface, by analysis in static mode with detection of negative (N-SIMS) and positive (P-SIMS) ions. We notice the presence of F, Cl, Na, these impurities result mainly from the sputtered target whereas the other elements H, O, C and the compound O-H result from the oil diffusion pump of the sputtering chamber. Figure 8, on the other hand, shows the SIMS profiling of some of these impurities where one observes a decrease in peak intensity as we get closer to the silicide-silicon interface. However a semi-quantitative concentration study of impurities , tungsten, or silicon was not feasible. This is due to fluctuations in the primary ions current and sputtering yields that change in presence of electronegative elements (Williams and Evans, 1978).

We did not observe a peak related to the compound WSi_x, so we performed a P-SIMS analysis under an oxygen atmosphere to increase the sputtering yields, i.e., the increase of the secondary ions current. We were able to observe peaks of very weak intensity corresponding to the compound WSi^+ only,as showed in Fig. 9. Apparently, the annealed surface thin film sputtering process leads to the same result as the composite target sputtering: Ejection of Si and W atoms essentially.

CONCLUSION

The results of surface analysis by using AES and XPS of tungsten silicide thin films show that these are covered with a very thin SiO_2 layer. After removing this oxide layer we have noticed the presence of argon in these films resulting from the sputtering chamber.The AES profiles of the thin films before and after annealing allows one to conclude that the native oxide layer (SiO_2) on the Si substrate does not present a diffusion barrier for Si to migrate from the substrate toward the thin film during annealing. As for the composition studies, they showed that thin films were tungsten rich with a concentration ratio Si:W less than 2.

Finally, even if the analysis by SIMS does not permit a quantitative study, it provides the impurity species which exist in the thin films. On the other hand, SIMS profiling shows the presence of F, Cl, Na , H, O and C

within the deposited thin films.These impurities result from the sputtered target and the sputtering chamber atmosphere. A comparative composition study of films obtained by other deposition techniques is necessary to obtain the degree of purity of the different deposited films.

ACKNOWLEDGMENT

H.K thanks the staff of the IMN laboratory in France where he prepared the samples and made the various measurements.

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