

Aluminium Diffusion in Titanium Nitride Films. Efficiency of TiN Barrier Layers

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Abstract. Two kinds of reactively evaporated titanium nitride films with columnar (B_0 films) and fine-grained (B_+ films) film structures, respectively, have been examined as diffusion barriers for preventing aluminium diffusion. The aluminium diffusion profiles have been investigated by 2 MeV $^4\text{He}^+$ Rutherford backscattering spectrometry (RBS) at temperatures up to 550° C. The diffusivity from 300° C to 550° C is: $D[\text{m}^2\text{s}^{-1}] = 3 \times 10^{-18} \exp[-30/(RT)]$ in B_0 layers and $D[\text{m}^2\text{s}^{-1}] = 1.4 \times 10^{-16} \exp[-48/(RT)]$ in B_+ TiN layers. The activation-energy values determined indicate a grain boundary diffusion mechanism. The difference between the diffusion values is determined implicitly by the microstructure of the layers. Thus, the porous B_0 layers contain a considerable amount of oxygen absorbed in the inter-columnar voids and distributed throughout the film thickness. As found by AES depth profiling, this oxygen supply allows the formation of Al_2O_3 during annealing the latter preventing the subsequent diffusion of the aluminium atoms.

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Due to the need to increase the packing density in VLSICs, thermally stable low-resistive contact and metallization technologies are becoming increasingly important inasmuch as high-temperature processes are applied. That is why substances other than aluminium are being considered as interconnection material. Nevertheless, aluminium is likely to continuously serve as the uppermost part of layered structures. To prevent junction failures due to aluminium–silicon interaction, diffusion barriers are used. The diffusion barrier under consideration in this paper is titanium nitride.

There has been considerable interest, since the early eighties, in refractory-metal nitride films, especially in titanium nitride, which has been investigated for applications within the microelectronics industry [1–7]. Titanium nitride thin films have been reported to be of interest in silicon technology particularly as diffusion barriers making possible reliable and thermally stable contacts in integrated circuits as well as in solar cells [8–13]. What is generally required of an effective contact barrier layer in the above-mentioned cases

is that it prevents the interaction between metal (contact material) and silicon in metallization schemes undergoing high-temperature processing and annealing. There are two interfaces where thermal stability must be ensured, namely the metal/barrier layer and barrier-layer/silicon interfaces. The barrier layer should interact either not at all or only slightly with the contact metal and the underlying silicon.

It is recognized that for barrier performance, in general, both structural (physical structure, structural defects) and chemical (metallurgical interactions) aspects play an important role. In the case under consideration no metallurgical interactions take place up to 600° C as it has been well established in the last decade [14–17]. The TiN barrier fails only above 600° C, due to the rise of reactions between aluminium and barrier material with reaction products intermetallic Al_3Ti and AlN . That is why the Al/TiN/Si barrier failure mechanism is diffusion-controlled up to 600° C and consequently the barrier efficiency can be estimated by means of the aluminium diffusivity in the TiN layer. Nevertheless, the authors are not aware of studies dealing with the quantitative estimation of aluminium diffusion in TiN layers. In papers dealing with the properties and applications of TiN, its barrier performance has been investigated and estimated on the basis of test structures and qualitative interpretation of RBS and AES spectra. This paper reports results on aluminium diffusivity, determined by RBS depth profiling of the diffused aluminium in TiN layers. The TiN layers studied have different physical structures and phase content and exhibit different permeability to aluminium atoms. It is worth to note here that, when actual aluminium metallization is being concerned, other factors, mainly mechanical properties, are of greater significance. Resulting from an intrinsic stress as well as from thermal mismatch between adjacent materials, aluminium penetrates easily through microcracks in the barrier, which enhances the Al–Si reaction and causes a barrier failure. For this reason an estimation of the barrier efficiency based only on the diffusivity has to be considered as provisional, keeping in mind that practical results can be considerably influenced by the technology adopted (deposition technique and conditions, post annealing procedures, etc.).

1 Titanium Nitride Layers

TiN layers have been deposited onto (100) silicon by reactive evaporation of Ti in an N_2 atmosphere. The deposition conditions were as follows: substrate temperature 60°C , background pressure 5×10^{-6} Pa, N_2 partial pressure 5×10^{-4} Pa and deposition rate of some 10^{-9} g $\text{cm}^{-2}\text{s}^{-1}$. Two kinds of TiN layers, about 80 nm thick, were deposited without or with ion bombardment during deposition, referred hereafter as the B_0 and B_+ layers, respectively. The ion-assisted deposition was achieved with Ar ions with an energy of 500 eV, at a ratio between the ion flux density and the metal flux density of 0.25; the Ar pressure was about 10^{-2} Pa. The deposition system has been described elsewhere [18]. After deposition the samples were stored in air for 20 h. Subsequently, a 70 nm aluminium layer was evaporated on the samples. The nitrogen-to-titanium ratio in the TiN layers is 1.0 and 1.15 for the B_0 and B_+ layers, respectively, as determined by AES, proposed by the authors and described in [19]. X-ray diffraction was used to study the phase composition and crystalline structure of the films. The B_0 films consist of δ -TiN, α -Ti and a phase composed of a rather disordered Ti-N compound, while the B_+ films consist of δ -TiN and Ti-N. All films were polycrystalline. The average grain size of the B_0 layers, as estimated from the halfwidth of the most pronounced (200) TiN and (011) Ti peaks by using Scherrer's equation, is respectively 25 nm and 20 nm. SEM measurements revealed a columnar growth of the B_0 layers. The columns are separated by voids, which occupy about a quarter of the layer volume. The B_+ films have a very dense microstructure with an average crystallite size of 10 nm [(200) TiN peak].

The TiN/Al/Si structures obtained have been annealed for 2 h at 300, 400, 500, and 550°C in flowing argon at atmospheric pressure.

2 Experimental Results and Discussion

Profiling of the TiN/Al/Si structures has been performed by RBS analysis with 2 MeV $^4\text{He}^+$ ions. The RBS spectra are evaluated using RUMP simulation [20]. The aluminium diffusivity was calculated from the penetration profiles, as already described in a previous paper [21]. Table 1 displays the results obtained. As far as the TiN layers are multiphase the so determined diffusivity corresponds to a combined effect of diffusion, described by the effective diffusivity D . The Arrhenius relationship for D was then calculated by best squares fit of the experimental results. Hence, for the

Table 1. Diffusivity results for Al diffusion in B_0 and B_+ TiN layers for 2 h annealing time

Annealing temperature [K]	Diffusivity [$\text{m}^2 \text{s}^{-1}$]	
	B_0 layers	B_+ layers
573	5×10^{-21}	5.5×10^{-21}
673	1×3.10^{-20}	2.5×10^{-20}
773	3×2.10^{-20}	6×10^{-20}
823	3×10^{-20}	1.4×10^{-19}

aluminium diffusion in TiN (B_0) and TiN (B_+) layer we obtain respectively:

$$D = 3 \times 10^{-18} \exp(-30/RT) \text{ m}^2\text{s}^{-1}$$

and

$$D = 1.4 \times 10^{-16} \exp(-48/RT) \text{ m}^2\text{s}^{-1}.$$

Generally, the possible mechanisms of diffusion are: bulk diffusion in material grains, diffusion in grain boundaries, surface diffusion in voids and pinholes and diffusion along dislocations in grains. The low values of the activation energy of aluminium diffusion in TiN layers (30–48 kJ mol^{-1}) supports the suggestion [22–24] that the main reasons for barrier failure is the diffusion via microscopic defects such as grain boundaries. Surprisingly, the B_0 titanium nitride layer, having porous columnar structure is a more efficient barrier than the B_+ layer – an unexpected result inasmuch as B_+ layers have a more densely packed structure. It must be mentioned here that such behavior of porous TiN layers in the Al/TiN/Si metallization scheme has been already observed by Sinke et al. [25] and Kumar et al. [26]. An inhibited (in comparison with TiN (B_+) layers) interdiffusion between TiN(B_0) and Y-Ba-Cu-O thin films has been recently ob-

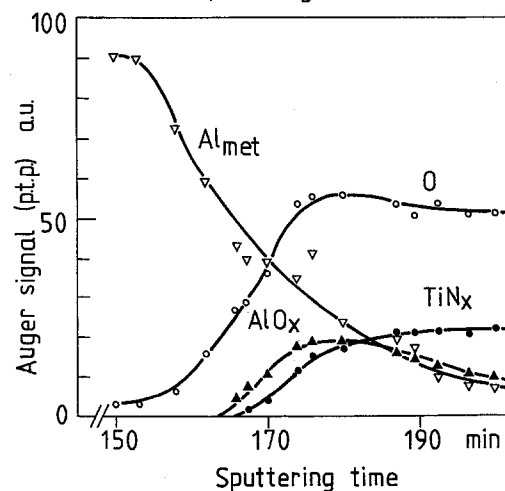
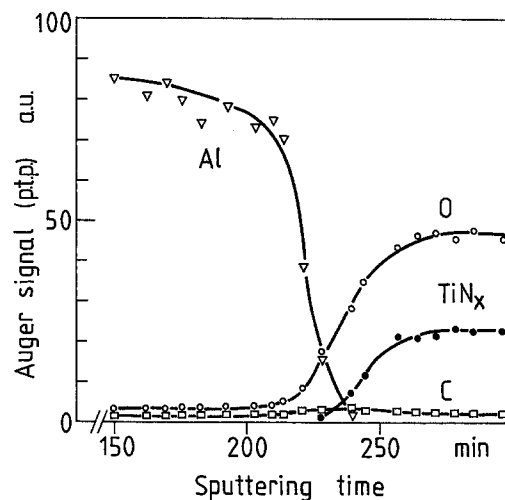


Fig. 1a, b. Auger depth profiles of Al/TiN (B_0)/Si structure (LMM transition of: Al in aluminium (Al_{met}) and alumina (AlO_x); Ti in titanium nitride (TiN_x)). **a** Nonannealed sample; **b** sample annealed for 2 h at 550°C

served by the authors [27]. The probable explanation of this phenomenon is related to the considerable amount of oxygen in B_0 layers, up to 20 at.%, compared with that in B_+ layers (about 2–4 at.%). This oxygen contamination takes place throughout the thickness of the film, probably due to voids in the B_0 layer. Actually, the voids enable the penetration of oxygen during film exposure to the atmosphere, either as O_2 or water vapour. One may assume that most of this oxygen is adsorbed on the columns and part of it diffuses along grain boundaries. It is presumed that this oxygen stock ensures the formation of oxides in the barrier zone upon annealing, in the form of Al_2O_3 , which is known to be efficient against Al diffusion. AES depth profiling confirms the formation of Al oxide. Thus, Fig. 1 displays the Auger depth profiles of two TiN (B_0) samples. While no alumina has been found in an unannealed sample (Fig. 1a), the sample annealed at 550° C exhibits the presence of Al_2O_3 , distributed in the whole barrier layer, as shown in Fig. 1b.

The efficiency of the B_+ barrier at 550° C is a factor of 2 less than that of the B_0 layer. Indeed, the mean penetration depth $d = 2(Dt)^{1/2}$ of Al in the B_+ barrier layer by annealing at 550° C for 30 min is 30 nm, while for the B_0 layer it is only 16 nm; thus, a B_0 barrier-layer thickness of 50–60 nm can be considered as high enough to ensure the barrier performance by 30 min annealing at 550° C. In the metallization scheme Al/TiN/Si, such a barrier thickness largely prevents the Al/Si interaction, the silicon penetration depth in the B_0 layer in such conditions being less than 20 nm [21].

3 Conclusion

The efficiency of titanium nitride layers for preventing aluminium diffusion has been investigated from 300° C to 550° C. The diffusivity of aluminium in porous TiN layers with voids and columnar structure (typical when deposited by reactive evaporation or reactive sputtering without bias) and in TiN layers with well-packed dense structure has been determined on the basis of RBS elemental depth profiling. The sufficiently low diffusivity of aluminium in the former type of TiN layers indicates that good diffusion barrier integrity in an Al/TiN(B_0)/Si structure could be ensured by a processing at temperatures up to 550° C.

References

1. M.A. Nicolet: *Thin Solid Films* **52**, 415 (1978)
2. C.I. Ting: *J. Vac. Sci. Technol.* **21** (1), 14 (1978)
3. J.P. Noel, D.C. Houghton, G. Este, F.R. Shepher: *J. Vac. Sci. Technol. A* **2** (2), 284 (1984)
4. M.F. Zhu, A.H. Hamdi, M.A. Nicolet: *Thin Solid Films* **119**, 5 (1984)
5. C.Y. Ting: *Thin Solid Films* **119**, 11 (1984)
6. S. Kanamori: *Thin Solid Films* **136**, 195 (1986)
7. J. Ding, Z. Liliental-Weber, E.R. Weber, J. Washburn, R.M. Forkas, N.W. Chang: *Appl. Phys. Lett.* **52** (25), 2160 (1988)
8. M. Wittmer: *Appl. Phys. Lett.* **37**, 540 (1980)
9. M. Mori, S. Kanamori, T. Ueki: *IEEE Trans. CHMT-6*, 159 (1983)
10. W.J. Garceau, P.R. Fournier, G.K. Herb: *Thin Solid Films* **60**, 237 (1979)
11. N.W. Cheung, H. von Seefeld, M.A. Nicolet, F. Ho, P. Iles: *J. Appl. Phys.* **52**, 4297 (1981)
12. M. Mäenpää, M.A. Nicolet, I. Suni, E.G. Colgan: *Sol. Energy* **27**, 283 (1981)
13. H. von Seefeld, N.W. Cheung, M. Mäenpää, M.A. Nicolet: *IEEE Trans. ED-27*, 873 (1980)
14. M. Wittmer: *J. Vac. Sci. Technol. A* **3** (2), 273 (1984)
15. M. Wittmer: *ibid.*, **A3** (4), 1797 (1985)
16. R.C. Ellwanger, J.M. Towner: *Thin Solid Films* **161**, 289 (1988)
17. N. Fujimura, N. Nishida, T. Ito, Y. Nakayama: *Mater. Sci. Eng. A* **108**, 153 (1989)
18. I.N. Martev, G.I. Grigorov, I.G. Petrov, E. Dynowska: *Thin Solid Films* **131**, 303 (1985)
19. J.L. Vignes, J.P. Langeron, G.I. Grigorov, I.N. Martev, M. Stoyanova: *Vacuum* **42**, 151 (1991)
20. L.R. Doolittle: *Nucl. Instrum. Methods B* **9**, 344 (1985)
21. K.G. Grigorov, G.I. Grigorov, M. Stoyanova, J.L. Vignes, J.P. Langeron, P. Denjean, J. Perriere: *Appl. Phys. A* **55**, 502 (1992)
22. N.W. Cheung, H. von Seefeld, M.A. Nicolet: In *Proc. of the Symposium on Thin Film Interfaces and Interactions*, ed. by J.E.E. Baglin, J.M. Poate (The Electrochem. Soc., Princeton, NJ 1980) p. 323
23. I. Suni, M. Mäenpää, M.A. Nicolet, M. Luomajärvi: *J. Electrochem. Soc.* **130**, 1215 (1983)
24. M. Finetti, I. Suni, M.A. Nicolet: *J. Electron. Mater.* **13**, 327 (1984)
25. W. Sinke, G.P.A. Frijlink, F.W. Saris: *Appl. Phys. Lett.* **47** (5), 471 (1985)
26. N. Kumar, K. Pourrezaei: *Thin Solid Films* **184**, 417 (1990)
27. K.G. Grigorov, G.I. Grigorov, M.V. Stoyanova, R.A. Chakalov, J.L. Vignes, J.P. Langeron, J. Perriere, P. Denjean: *Vacuum* (in press)