AIP | Applied Physics Letters

Thermal oxidation of tantalum silicide in O2 and H2O

Krishna C. Saraswat, Ronald S. Nowicki, and John F. Moulder

Citation: Applied Physics Letters **41**, 1127 (1982); doi: 10.1063/1.93424
View online: http://dx.doi.org/10.1063/1.93424
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/41/12?ver=pdfcov
Published by the AIP Publishing

Thermal oxidation of tantalum silicide in O_2 and H_2O

Krishna C. Saraswat
Department of Electrical Engineering, Stanford University, Stanford, California 94305
Ronald S. Nowicki[a] and John F. Moulder[a]
Perkin–Elmer, Surface Science Division, Mountain View, California 94043

(Received 1 June 1982; accepted for publication 27 September 1982)

Thermal oxidation of $TaSi_2$ in dry oxygen and steam has been investigated. 0.3-μm-thick films of tantalum silicide were deposited by cosputtering on high resistivity ⟨111⟩ silicon and oxidized silicon wafers. After a crystallization anneal in argon, the films were oxidized in dry O_2 or steam at 1000 and 1100 °C. In all cases oxidation was observed. For $TaSi_2$ deposited on Si, only the growth of SiO_2 was observed, indicating that the Si diffused through $TaSi_2$ before oxidation, and $TaSi_2$ remained intact. In the case where $TaSi_2$ was deposited on SiO_2, it was actively involved in the oxidation process, resulting in the formation of SiO_2 and Ta_2O_5.

PACS numbers: 81.60. – j

Continual advancements in integrated circuits technology are resulting in smaller device dimensions and increased chip area. Because of this, the interconnection lines have become very long, and the time delays associated with the parasitic capacitance and resistance can become appreciable. Thus, even with small and therefore very fast devices, the overall performance of a large circuit could be seriously affected by the *RC* delays of the interconnections.[1] Proper selection of material within the constraints of fabrication technology can result in minimization of *RC* delay time. Polycrystalline silicon has been used in this situation, but its high resistivity results in very high *RC* delay time. Composites of polycrystalline silicon and silicides of Mo, W, Ti, and Ta have been proposed as alternatives to polycrystalline silicon.

In a multilayer interconnection technology, the layers incorporated early in processing are required to be able to be thermally oxidized in O_2 and H_2O. Several investigations have been made which study the thermal oxidation of these silicides, and it has generally been found that silicides of W, Mo, and Ti are thermally oxidized in O_2 and H_2O ambients.[2–5] However, some controversy exists about the kinetics of the oxidation of $TaSi_2$. Murarka *et al.*[6] observed that the oxidation of $TaSi_2$/poly-Si composite structure occurs readily in H_2O, but is negligible in an O_2 ambient. Our prior work,[7] and that of others,[8,9] to the contrary indicate that oxidation occurs in both ambients. In this work we have attempted to obtain a better understanding of the oxidation behavior of $TaSi_2$.

The $TaSi_2$ films were deposited by simultaneous rf diode sputtering of Ta and Si from high-purity targets. The details of the technique are described in the literature.[10] The data presented here are for 0.3-μm-thick silicide films, deposited on high resistivity ⟨111⟩ oriented silicon and oxidized silicon wafers. Auger electron spectroscopy and electron microprobe analysis indicated that in the as-deposited films the atomic ratio between Si and Ta was approximately 2:1. X-ray diffraction analysis showed no specific peaks of Ta, Si or $TaSi_2$, indicating that the as-deposited films were amorphous. Therefore, prior to the oxidation the samples were annealed at the oxidation temperature (1000 or 1100 °C) in argon for 10 min to homogenize and crystallize the structure of $TaSi_2$. The annealing resulted in polycrystalline films of $TaSi_2$ free of any marked preferred orientation. Following the anneal, the samples were oxidized according to three different conditions: (1) 60 min in dry O_2 at 1000 °C; (2) 60 min in dry O_2 at 1100 °C; (3) 10 min in steam (Ar bubbled through 95 °C H_2O) at 1000 °C. Following the oxidation, the wafers were annealed for 10 min in Ar and slowly pulled out of the furnace. The oxidized samples were examined by Auger electron spectroscopy, x-ray diffraction, and scanning electron microscopy.

In all cases, i.e., in O_2 and H_2O ambients and on $TaSi_2$/Si and $TaSi_2/SiO_2$ structures, thermal oxidation was ob-

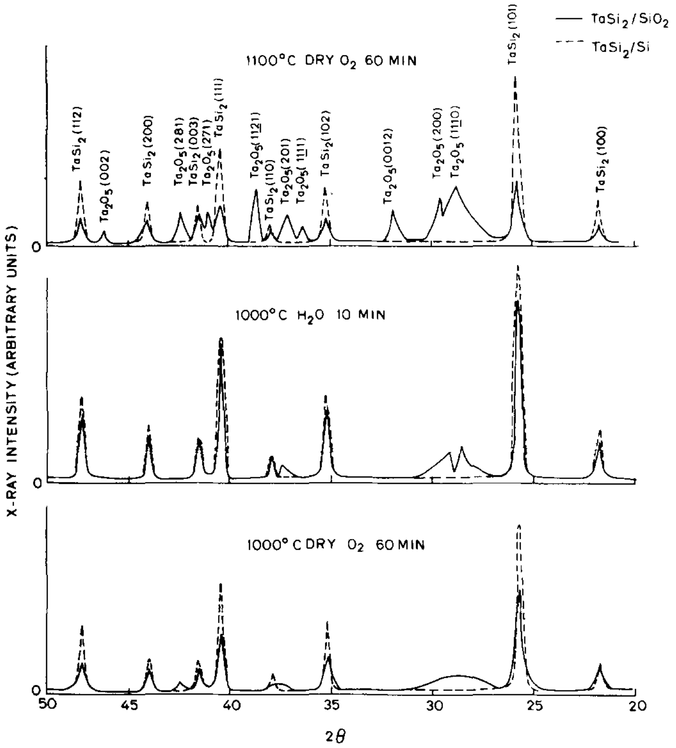

FIG 1. X-ray diffraction pattern of the oxidized tantalum silicide films.

---

[a] Present address: Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94303.

served. The scanning electron micrographs showed that the resulting surface was very rough for the oxidation of $TaSi_2$/SiO_2 samples, and in some cases cracks and lifting of the films from the substrate was observed. The surface was considerably smoother in the case of $TaSi_2$/Si oxidation and no cracks or lifting was observed.

All the samples were analyzed by the x-ray diffraction technique in which the film texture was obtained by measuring the diffracted intensity of an x-ray beam at twice the angle of incidence of the beam from a 20-keV copper radiation. The results are shown in Fig. 1. In the case of $TaSi_2$/Si samples, only $TaSi_2$ diffraction peaks were observed, whereas for $TaSi_2$/SiO_2 samples, additional diffraction peaks of Ta_2O_5 were also observed. No other phase of tantalum silicide was observed. By comparing the diffraction profiles at 1100 °C oxidation with the 1000 °C oxidation it can be deduced that at the higher oxidation temperature in the case of $TaSi_2$/SiO_2 samples, the intensity of $TaSi_2$ diffraction peaks reduced and those of Ta_2O_5 increased. No Ta_2O_5 formation could be detected in any of the annealed but not yet oxidized samples. The diffraction patterns of the annealed but not yet oxidized samples were very similar to those shown in Fig. 1 for $TaSi_2$/Si samples and are therefore not reproduced here.

The samples were further examined by the Auger sputter profiling technique, and the results are shown in Figs. 2 and 3. It can be seen in both the figures that the bulk of the oxidized layers contains only silicon and oxygen, and within the resolution of the Auger spectrometer, no tantalum could be measured in the grown films. By comparing these Auger profiles to those of known SiO_2 thermally grown on silicon, it was confirmed that the grown films were indeed stoichiometric SiO_2. It is evident that $TaSi_2$ can be thermally oxidized in dry oxygen with and without the presence of free silicon underneath. Considerable broadening of the $TaSi_2$/Si and $TaSi_2$/SiO_2 interface can be served in Figs. 2 and 3 and it increases with the thickness of the grown SiO_2. This broad-

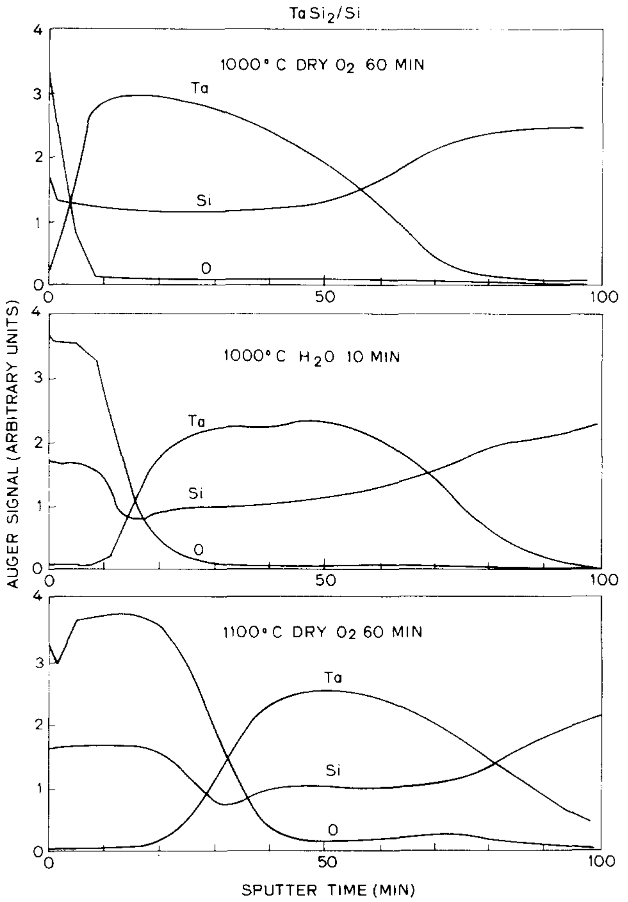

FIG. 2. Auger sputter profiles of tantalum silicide films deposited on ⟨111⟩ silicon and oxidized at (a) 1000 °C in dry O_2 for 60 min, (b) 1000 °C in H_2O for 10 min, and (c) 1100 °C in dry O_2 for 60 min.

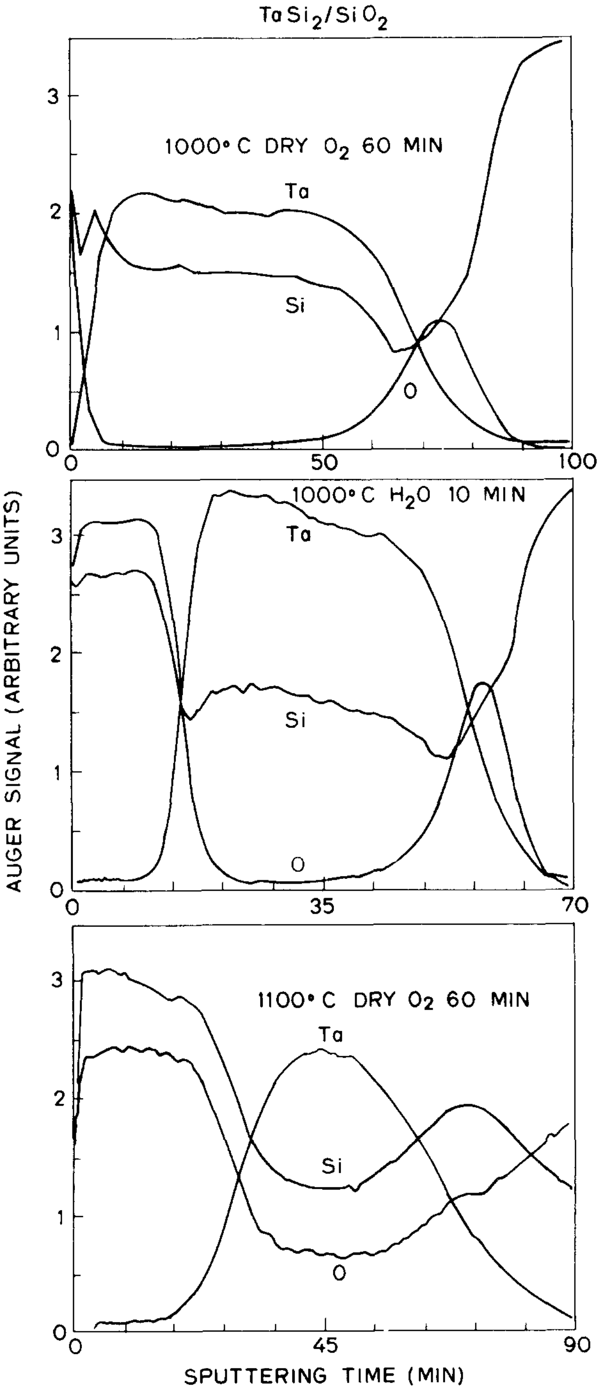

FIG. 3. Auger sputter profiles of tantalum silicide films deposited on oxidized silicon at (a) 1000 °C in dry O_2 for 60 min, (b) 1000 °C in H_2O for 10 min, and (c) 1100 °C in dry O_2 for 60 min.

ening could be partly attributed to artifact of the measurement technique, but partly also to interface roughening, as also pointed out by Razouk *et al.*[8]

By combining the results of x-ray diffraction and Auger sputter profiling, certain conclusions can be drawn regarding the mechanism of oxidation. For the oxidation of $TaSi_2$ deposited on silicon (Fig. 2), as the oxidation proceeds, the entire layer of $TaSi_2$ is displaced towards the substrate without any change in its thickness. From the x-ray diffraction results, we concluded earlier that no change in the crystal structure of the $TaSi_2$ was observed. This indicates that as long as free Si is available underneath the silicide, Ta is not oxidized at all. At the temperature of oxidation, Si is highly mobile in other silicides[2–5] and it is reasonable to assume that it diffuses rapidly in $TaSi_2$ also. Thus, as the oxidation proceeds, silicon diffuses through the $TaSi_2$ and is oxidized by O_2 or H_2O. The composition of $TaSi_2$ remains unchanged.

The situation is more complex if free silicon is not available. From the Auger sputter profiling (Fig. 3) it can be seen that a layer of SiO_2 is grown on top of the silicide; however, the x-ray diffraction analysis (Fig. 1) shows that formation of Ta_2O_5 is accompanied with that of SiO_2. Since no free silicon is available for oxidation, it is reasonable to assume that tantalum silicide is oxidized into Ta_2O_5 and SiO_2

$$TaSi_2 + O_2 \rightarrow Ta_2O_5 + SiO_2.$$

A similar reaction should take place with H_2O. Similar reactions have been observed in the oxidation of WSi_2,[2,3] $MoSi_2$,[11] and $TiSi_2$[5] deposited on SiO_2. Since no tantalum was detected in the bulk of the grown SiO_2, the Ta_2O_5 probably remains at the interface, or right next to it in the silicide layer. As the oxidation proceeds, more Ta_2O_5 is formed as the x-ray diffraction results show (Fig. 1).

In general, these results are similar to the oxidation of other silicides[2–5] but differ from the observation of Murarka *et al.*,[6] where no oxidation of $TaSi_2/Si$ was observed in dry O_2. In that case, the silicide was formed by depositing Ta on Si and then sintering. This could have resulted in a silicide of different properties.

In summary, we have shown that $TaSi_2$ can be thermally oxidized in dry O_2 and H_2O at 1000 and 1100 °C. If free silicon is present underneath the $TaSi_2$, it diffuses through the silicide and is oxidized to produce SiO_2. In the other case, where no free silicon is present, $TaSi_2$ is directly oxidized to form SiO_2 and Ta_2O_5.

[1] K. C. Saraswat and F. Mohammadi, IEEE Trans. Electron. Devices **ED-29**, 645 (1982).

[2] S. Zirinski, W. Hammer, F. d'Heurle, and J. Baglin, Appl. Phys. Lett. **33**, 76 (1978).

[3] F. Mohammadi, K. C. Saraswat, and J. D. Meindl, Appl. Phys. Lett. **35**, 529 (1979).

[4] T. Inoue and K. Koike, Appl. Phys. Lett. **33**, 826 (1978).

[5] J.-R. Chen, M.-P. Houng, S.-K. Hsiung, and Y. -C. Liu, Appl. Phys. Lett. **37**, 824 (1980).

[6] S. P. Murarka, D. B. Fraser, W. S. Lindenberger, and A. K. Sinha, J. Appl. Phys. **51**, 3241 (1980).

[7] K. C. Saraswat, R. S. Nowicki, and J. F. Moulder, Abstract from the Technical Program of the Electronics Materials Conference, Santa Barbara, California, June 24–26, 1981.

[8] R. R. Razouk, M. E. Thomas, and S. L. Pressacco, J. Appl. Phys. **53**, 5342 (1982).

[9] D. Pawlik, E. Doering, and H. Oppolzer, Extended Abstracts 161st Meeting of the Electrochemical Society, May 1982, Montreal, Abstract No. 195.

[10] R. S. Nowicki and J. F. Moulder, J. Electrochem. Soc. **128**, 562 (1981).

[11] J. B. Berkowitz-Mattuck and R. K. Dils, J. Electrochem. Soc. **112**, 583 (1965).