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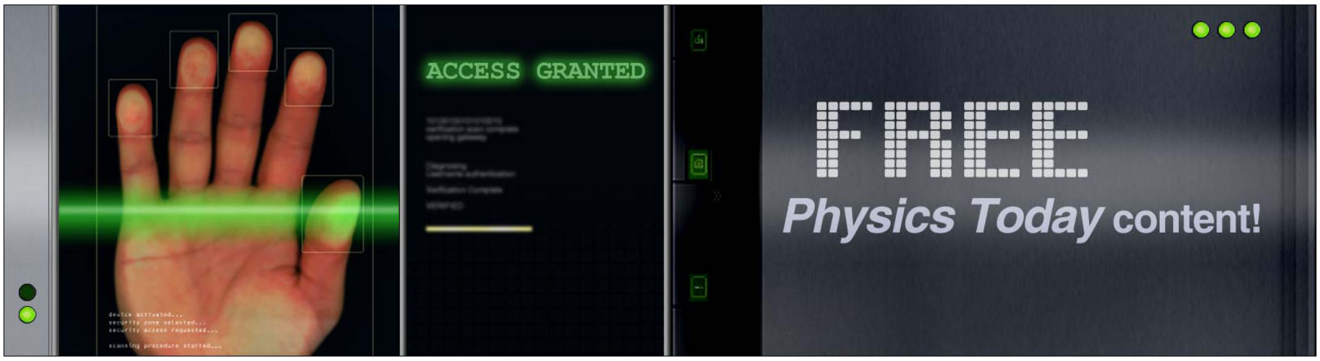

Oxidation of silicide thin films: $TiSi_2$

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The oxidation of $TiSi_2$ thin films on polysilicon illustrates extreme examples of behavior. At 700 °C in wet O_2, one observes the formation of titanium oxide and the simultaneous rejection of silicon towards greater depths, away from the oxidized surface layer. At 1100 °C with the same type of sample, one observes the growth of a metal-free layer of SiO_2, the formation of which required not only the use of the whole available polysilicon, but the reduction of the initial disilicide to a lower silicide, mostly TiSi. These observations are discussed in terms of previous results obtained either with $TiSi_2$ or with other silicides, and in terms of what is known about the thermodynamics of the system titanium oxide-silicon oxide.

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The importance of $TiSi_2$ and of its oxidation behavior is derived from its low resistivity (measurements of 15 $\mu\Omega$ cm compare well with earlier reports[1]) and its potential use as a conductor in microelectronics. In addition, one's scientific curiosity is aroused by the description[2] of the oxidation behavior of $TiSi_2$ as being different from that of other silicides; the SiO_2 formed would always contain titanium in amounts clearly detectable by Rutherford backscattering. Moreover, the silicon in such metal-rich SiO_2 would come from the substrate and not from the silicide.[3] This implies the efficacy of a somewhat unexpected bypass (perhaps grain boundary) diffusion mechanism. However, since it is known[4–6] that $TiSi_2$ forms as a result of the motion of silicon atoms at temperatures as low as 600 °C, there appears to be no need to invoke short circuits for the diffusion of silicon during the oxidation of $TiSi_2$ at temperatures in excess of 700 °C.

An interesting publication[7] on the oxidation of $HfSi_2$ implies that for this silicide, the failure to obtain a clean layer of pure SiO_2 results from the ability of the metal, to reduce SiO_2. One may visualize the reaction at the silicide-oxide interface, during SiO_2 formation: the silicide is decomposed, the silicon reacts with oxygen to form SiO_2, and excess metal atoms are liberated. Atoms which can react with SiO_2 are likely to display a behavior different from those which cannot reduce SiO_2. Undoubtedly, this plays a significant role in the great ease encountered in oxidizing such silicides as $CoSi_2$ and $NiSi_2$. But the matter is not so simple. To begin with, it is clear that the heat of formation of the silicides is small (32 kcal/mole for $TiSi_2$)[8] smaller indeed than the heat of formation of the respective metal oxides (including the platinum metals) so that from a purely thermodynamic point of view, equilibrium would in all cases call for the total dissociation of the silicides and the simultaneous formation of both metal and silicon oxides. That this is usually not observed points out the important role of kinetic factors. One knows that in the formation of SiO_2 on silicon, the main limiting factor in the process is the diffusion of oxygen through the oxide layer. One also knows that in general, the rate of oxidation of the silicides is somewhat greater than that of pure silicon (a factor varying about a value of 2). Thus, if we neglect the possibility of great structural modifications of the nature of the oxide over silicide layers, the oxidation of these layers would be limited by a relative paucity of oxygen at the silicide-oxide interface. The evidence at hand indicates that usually the reaction between silicon and oxygen is quite rapid. What happens to the metal atoms is then again dictated by kinetics. Provided the rate of diffusion through the silicide is sufficiently high, the metal can often react with silicon, to maintain the integrity of the silicide layer, faster than it can be oxidized, and faster than it can reduce SiO_2. Such a behavior has been observed with WSi_2.[9,10] The key point is that diffusion through the silicide layer should be fast, which sets two requirements on the oxidation process. Firstly, the oxidation temperature should preferably be significantly higher than the temperature at which the silicides can be formed (a factor which might be more important in the easy oxidation of $CoSi_2$ or NiSi, than the relatively low heats of formation of the respective oxides). Secondly, great care must be exercised in oxidizing silicide layers so that no oxidation takes place at temperatures below the desired oxidation temperature. This means that the samples should always be brought to temperature in a totally inert atmosphere, and only when the samples have reached thermal equilibrium should the oxidizing atmosphere be introduced.[11]

The oxidation behavior of $TiSi_2$ in wet oxygen bubbled through water at 30 °C was investigated with two sets of samples: single crystal silicon and polysilicon on oxidized silicon wafers [1000-Å thermal oxide and 300-Å chemical vapor deposited (CVD) polysilicon]. The polysilicon wafers were saturated with phosphorus through the usual $POCl_3$ treatment and drive-in, respectively: 870 °C 15 min and 1000 °C 10 min. A film of titanium 1000 Å thick was deposited on all samples at room temperature using vacuum evaporation at a pressure in the high 10^{-7} Torr range. The silicide was formed by heat treatment at 700 °C for one hour in an atmosphere of argon. The procedure of preheating the samples in an inert atmosphere, which was outlined above, was strictly followed. After introduction of the samples in the oxidizing furnace, the tube was flushed with argon for 30 min, then the samples were introduced in the hot zone of the furnace and argon flushing was continued for another fifteen minutes. Analysis of the oxidized layer was carried out

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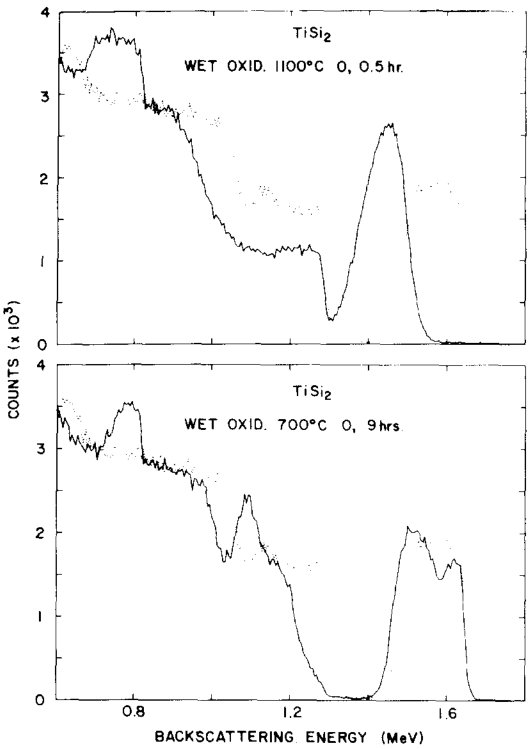

FIG. 1. Backscattering spectra illustrating the oxidation behavior of $TiSi_2$ films grown on polycrystalline silicon over thermally oxidized Si wafers, plain lines and dashed lines, respectively, after oxidation and as formed (by metal-silicon reaction). On top oxidation at 1100 °C for 0.5 h. At the bottom oxidation at 700 °C for 9 h, both in O_2 bubbled through water.

through Rutherford backscattering. The results in Fig. 1 illustrate two extreme behavior observed with the polysilicon samples. At 700 °C no SiO_2 was formed, but there was considerable oxidation of the titanium. Indeed in this case the silicon was rejected and was found to have accumulated at the silicide-polysilicon interface. There is a small layer of $TiSi_2$ left after the 9-h oxidation treatment. Oxidation at 1100 °C resulted in a totally different behavior: the formation of a thick layer of SiO_2 quite free from titanium, the total consumption of the thin layer of polysilicon left after silicide formation, and the reduction of $TiSi_2$ to a lower silicide with a composition corresponding to about TiSi. (Given the respective heats of formation, − 31 kcal/mole for TiSi and − 32 kcal/mole for $TiSi_2$,[8] the reduction of $TiSi_2$ to TiSi should be easy). In Fig. 2 one sees only the titanium part of the backscattering spectra, for single crystal samples before oxidation, and after different oxidizing treatments. The results obtained at 750 °C are quite identical to those in Fig. 1 at 700 °C. At 800 °C, a layer of SiO_2 has been formed, but it still contains a significant amount of titanium. At 900 °C, the presence of residual titanium has almost totally disappeared. Figure 3 shows that a considerable layer of SiO_2 can be grown at 950 °C, with only a trace of included titanium.

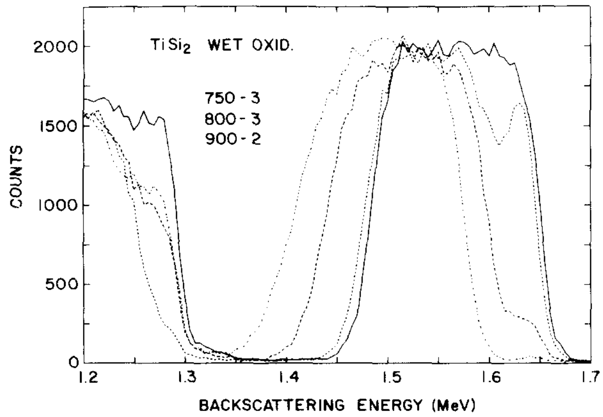

FIG. 2. Part of the backscattering spectra of $TiSi_2$ formed by metal-silicon reaction, respectively, as reacted, and after oxidation at 750 °C for 3 h, 800 °C for 3 h also, and 900 °C for 2 h.

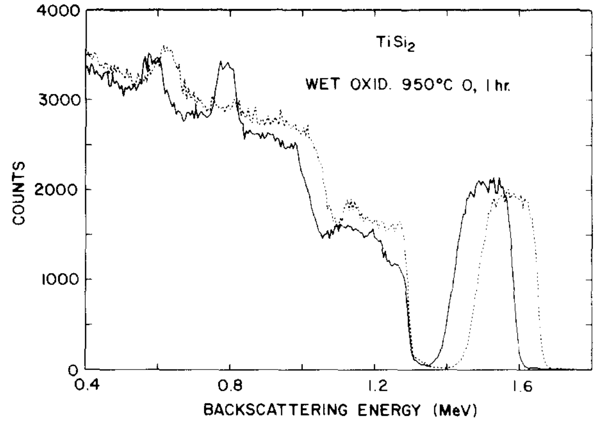

FIG. 3. Backscattering spectra of $TiSi_2$ films (over an oxidized Si wafer, as in Fig. 1), respectively as formed, and after oxidation at 950 °C for 1 h.

The dramatic change one observed as a function of increased temperature is almost entirely a matter of kinetics, and not one of thermodynamics. In Fig. 4 one finds a plot of the free energy of SiO_2 and various oxides of titanium from room temperature to 1200 °C. For the purpose of compari-

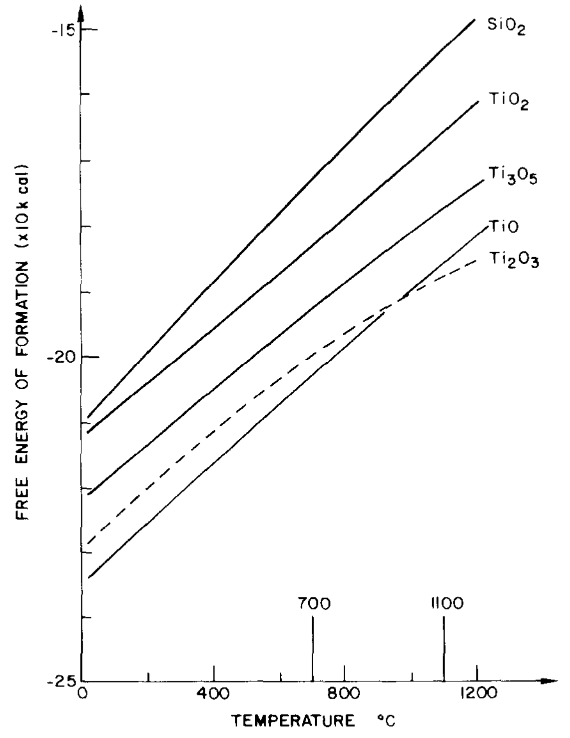

FIG. 4. Free energies of formation, per mole of O_2, respectively, for amorphous SiO_2 and for various oxides of Ti.

son, the data which were calculated from published tables[12] have been normalized to one mole of oxygen. There are no significant changes in the relative positions of the curves in the interval 700–1200 °C. The line for amorphous SiO_2 was extrapolated from high-temperature data for liquid SiO_2, yet the overall relative picture is the same as that published by others for SiO_2 and TiO_2.[13]

It is possible to obtain SiO_2 relatively free of titanium provided the temperature is above 900 °C (in wet oxygen). The oxidation behavior of silicides seems to be mostly a matter of kinetics with thermodynamic considerations playing only a secondary role. The absence of the formation of metal oxide appears to depend on the rapid formation of SiO_2 and the resulting exhaustion of available oxygen. Figure 2 focuses one's attention on the requirements to avoid oxidation during the period when the samples are heated to oxidation temperatures in excess of 900 °C. With such silicides as WSi_2 and $MoSi_2$, given the tendency of the metals to form so lattice oxides, tell tale traces of metal oxidation during heating may disappear, but with $TiSi_2$ once titanium oxides are formed, they remain. The failure to follow careful heating procedures seems to have marred the results obtained by previous investigators[2,3] and may invalidate their conclusion about the diffusion of silicon during the oxidation of $TiSi_2$.

Water vapor reduces the role of the interface reaction rate factor in the oxidation of silicon, so that even for thin oxide layers, diffusion becomes rate limiting.[14] It is intriguing to think that the "catalytic" effect of water vapor in enhancing the formation of SiO_2 bonds, may be precisely the factor responsible for the often observed effect that the oxidation of silicide layers (meaning here the formation of metal-free SiO_2) is almost always easier with a wet atmosphere.[15] This explanation does not necessarily imply that water vapor would not enhance the rate of reaction between metal and oxygen, only that the effect would be greater in the case of silicon than in that of the metals. The formation of an even layer of SiO_2 on the surface of a silicide should require not only a ready supply of silicon atoms, but also that these atoms should react with oxygen faster than the metal atoms.

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[1] S. P. Murarka, M. H. Read, C. J. Doherty, and D. B. Fraser, J. Electrochem. Soc. **129**, 293 (1982).
[2] Jiann-Ruey Chen, Man-Phon Hong, Shen-Kan Hsiung, and Yuen-Chung Liu, Appl. Phys. Lett. **37**, 824 (1980).
[3] Jiann-Ruey Chen, Yuen-Chung Liu, and Sheng-Deh Chu, Appl. Phys. Lett. **40**, 263 (1982).
[4] S. P. Murarka and D. B. Fraser, J. Appl. Phys. **51**, 342 (1980).
[5] W. K. Chu, S. S. Lau, J. Mayer, H. Muller, and K. N. Tu, Thin Solid Films **25**, 393 (1975).
[6] F. d'Heurle and C. Y. Ting (unpublished).
[7] S. P. Murarka and C. C. Chang, Appl. Phys. Lett. **37**, 639 (1980).
[8] A. Searcy and L. Finnie, J. Amer. Ceramic Soc. **45**, 268 (1962).
[9] J. Baglin, F. d'Heurle, and S. Petersson, Appl. Phys. Lett. **33**, 289 (1978).
[10] S. Zirinsky, W. Hammer, F. d'Heurle, and J. Baglin, Appl. Phys. Lett. **33**, 76 (1978).
[11] J. Baglin, F. d'Heurle, and S. Petersson (unpublished).
[12] *Handbook of Chemistry and Physics*, 49th ed. (Chemical Rubber, Cleveland, 1968), pp. D-34 to D-37.
[13] L. Darken and R. Gury, *Physical Chemistry of Metals* (McGraw–Hill, New York, 1953), p. 349.
[14] E. Irene, J. Electrochem. Soc. **125**, 1709 (1978).
[15] F. Mohammadi, K. Saraswat, and J. Meindl, Appl. Phys. Lett. **35**, 529 (1979).

Quantum transport in a single layered structure for impurity scattering

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In this letter we present results for the mobility of electrons confined in a layered structure when the scattering of the confined carriers is dominated by ionized impurity scattering. In the size quantum limit, the mobility is found to decrease with the layer thickness in contrast to the situation where acoustic phonon scattering is dominant. In the latter case, the mobility is found to increase with the layer thickness. We have considered the effects of both background and remote impurities on the mobility of the confined carriers. The results which we have obtained are considerably different from those currently available in the literature.

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In recent years, there has been a growing interest in layered structures such as semiconducting thin films,[1–3] space-charge inversion layers,[3,4] and synthetic semiconductor superlattices.[5–7] The reason for this growing interest is the increasing technological importance of these structures. Modulation-doped $Al_xGa_{1-x}As$ heterostructures have been grown using epitaxial techniques, and high mobilities have been reported in these structures.[7,8] In these structures, the carriers form a quasi-two-dimensional electron gas

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