JOURNAL OF MATERIALS SCIENCE 25 (1990) 98–102

The effect of amorphous silicon capping on titanium during $TiSi_2$ formation by RTA

S. W. KANG, S. C. PARK
Electronics and Telecommunications Research Institute, PO Box 8, Daedog Danji, Daejeon, Chungnam, 300-32, Korea

S. CHUN
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

Thin film reactions of the Ti/(1 0 0)Si structure and the amorphous-Si/Ti/(1 0 0)Si structure are performed by rapid thermal annealing (RTA) in argon at temperatures of 500–800° C. Auger depth profiling shows that the as-deposited titanium film of the Ti/(1 0 0)Si structure and the as-deposited amorphous silicon (a-Si) film of the a-Si/Ti/(1 0 0)Si structure exhibit a roughly exponential oxygen distribution decreasing from the surface when exposed to air. An electronic spectroscopy for chemical analysis (ESCA) shows that the oxygen in the a-Si film forms SiO_2 and the oxygen in the titanium film forms titanium oxide. For the Ti/(1 0 0)Si structure, the oxygen tends to be redistributed uniformly throughout the titanium film near the onset of silicide formation during RTA. As silicide formation progresses, the redistributed oxygen is snowplowed back toward the surface owing to oxygen solubility difference between Ti and $TiSi_2$. Consequently, the oxygen concentration in the unreacted titanium layer increases. This increased oxygen concentration retards the silicide growth even though there remains an unreacted titanium layer. The oxygen redistribution in the titanium film correlates well with the rapid increases in the sheet resistance near the onset of silicide formation. When a-Si is sputter-deposited sequentially on the titanium film without breaking the vacuum, the oxygen in a-Si is not redistributed during RTA. Thus there is no rapid increase in the sheet resistance, and the saturated sheet resistance is lower than that of Ti/(1 0 0)Si structure. The reason is that the conversion of deposited titanium film into $TiSi_2$ is made completely because the a-Si film on the titanium film prevents oxygen infiltration into the titanium film.

1. Introduction

Owing to the advantages of its lower resistivity along with the high temperature stability, $TiSi_2$ has been used on the source/drain regions for the self-aligned contacts and/or on the polysilicon film for the interconnections in advanced metal-oxide-semiconductor field effect transistor (MOSFET) structures. Recently $TiSi_2$ has been applied to a polysilicon self-aligned (PSA) emitter to obtain lower emitter resistance for high speed bipolar devices. As an interconnection, the parameter of primary concern is the sheet resistance. For the self-aligned source/drain contacts, the parameter of primary interest is the contact resistance. As with many of the silicides which have been formed by a direct reaction of silicon with a reactive metal, the residual gas content in the metal film and in the annealing ambient can have a pronounced effect on the silicide formation [1]. In particular, titanium is highly reactive with oxygen, being capable of containing up to 30 at % oxygen [2]. The presence of oxygen in a titanium film is an important factor in the irreproducibility of the reaction between titanium and silicon. Several studies have investigated the behaviour of oxygen during silicide formation [3–7]. It has been found that $TiSi_2$ does not take in oxygen but pushes it away to the unreacted titanium layer, because oxygen is more soluble in titanium than in $TiSi_2$. It is known as the snowplow effect. Hence, in the present study a-Si film is deposited on titanium film to protect the titanium film from the oxygen impurity when exposed to air and annealed at high temperature. We studied the role of the a-Si layer on the formation of $TiSi_2$ by examining the reaction of the titanium film on a (1 0 0) oriented silicon substrate and the reaction of the titanium film sandwiched between (1 0 0) oriented silicon substrate and a-Si overlayer using RTA. The films were characterized before and after RTA with Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA) and sheet resistance measurements.

2. Experimental procedure

The starting substrates were (1 0 0) p-type silicon wafers having a resistivity of 6–8 Ω cm. Immediately prior to titanium deposition the samples were sputter-etched in a radio frequency (RF) plasma discharge using argon gas. Titanium films were then deposited by magnetron sputttering using a 99.91% pure titanium

0022-2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

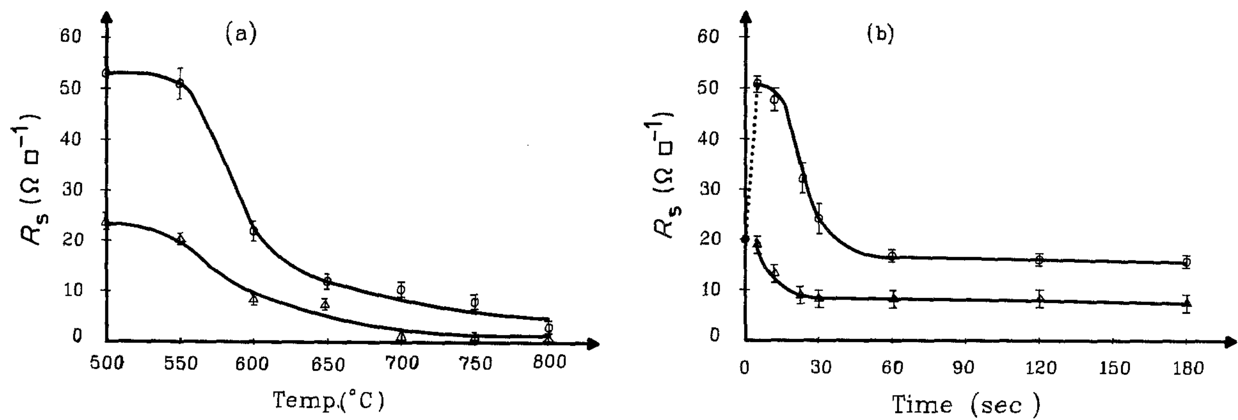

Figure 1 The dependence of sheet resistance R_s on the two sample structures: (Φ) Ti/(1 0 0)Si structured sample and (Å) a-Si/Ti/(1 0 0)Si structured sample. The sheet resistance is given as a function of (a) annealing temperature, and (b) annealing time at 600° C.

target in an argon atmosphere at a pressure of 6.4×10^{-3} torr. The titanium deposition rate was $1.7\,nm\,sec^{-1}$. The deposited titanium film thickness was determined to be 50 nm. The as-deposited sheet resistance of the titanium film was $19.5\,\Omega\,sq^{-1}$. In some cases, 30 nm of a-Si film was sputter-deposited on 50 nm titanium film sequentially at a rate of $1.6\,nm\,sec^{-1}$ without breaking vacuum, using a boron doped silicon target. The as-deposited sheet resistance of a-Si/Ti bilayer was $21.3\,\Omega\,sq^{-1}$. The samples were annealed in an argon atmosphere by RTA for 5–180 sec at temperature ranging from 500 to 800° C. Then the samples were analysed by AES depth profiling. Sheet resistance was measured with a four-point probe. Also, ESCA was used to evaluate the chemical state of oxygen in the titanium film and in the a-Si film.

3. Results and discussion

Figure 1 shows the sheet resistance of Ti/(1 0 0)Si structured sample and a-Si/Ti/(1 0 0)Si structured sample measured by conventional four-point probe, as a function of annealing temperature and time. The downward trend of sheet resistance is the result of the silicide formation as evidenced by Auger depth profile, which will be discussed later. For Ti/(1 0 0)Si structured sample, the sheet resistance after 5 sec annealing at 600° C by RTA reaches to the maximum and then continues to decrease as the silicide growth processes. The saturated sheet resistance is $18\,\Omega\,sq^{-1}$. For the a-Si/Ti/(1 0 0)Si structured sample, the rapid increase of sheet resistance is not observed and the saturated sheet resistance is $9\,\Omega\,sq^{-1}$. We attribute these sample structure dependences of sheet resistance to the oxygen impurity distribution in the unreacted titanium film as shown in Figs 2 and 3. Figure 2 shows the Auger depth profiles of the as-deposited films of Ti/(1 0 0)Si structure and a-Si/Ti/(1 0 0)Si structure. The concentration of oxygen at the surface of the titanium film and the a-Si film reaches up to 40–50 at %. The as-deposited films exhibit a roughly exponential oxygen distribution, decreasing from the film surface. This exponential distribution of oxygen from the film surface indicates that the sample exposed to air takes in oxygen at the surface. The total oxygen in titanium film of the Ti/(1 0 0)Si structure is more than that in a-Si film of a-Si/Ti(1 0 0)Si structure. This suggests that the titanium film is more reactive with oxygen than the a-Si film when exposed to air. However, the oxygen is confined in a very thin layer near the surface and the remaining part of the as-deposited film is free of oxygen. Figure 3 shows the Auger depth profiles of the Ti/(1 0 0)Si structured sample rapidly annealed at 600° C for different annealing time. After 5 sec annealing at 600° C, the oxygen is very uniformly distributed throughout the titanium film (about 12 at %). As silicide growth progresses, the oxygen is expelled by the advancing silicide front, and oxygen is not measured in $TiSi_2$ within the detection limit of

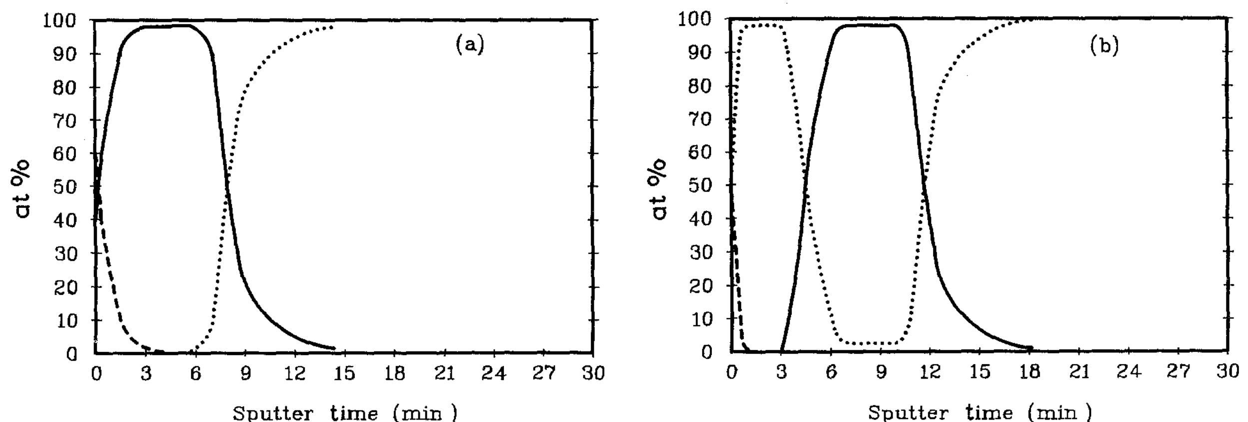

Figure 2 AES depth profiles of the as-deposited films when exposed to air: (a) Ti/(1 0 0)Si; (b) a-Si/Ti/(1 0 0)Si. (——) Titanium; (· · · ·) silicon; (– – –) oxygen.

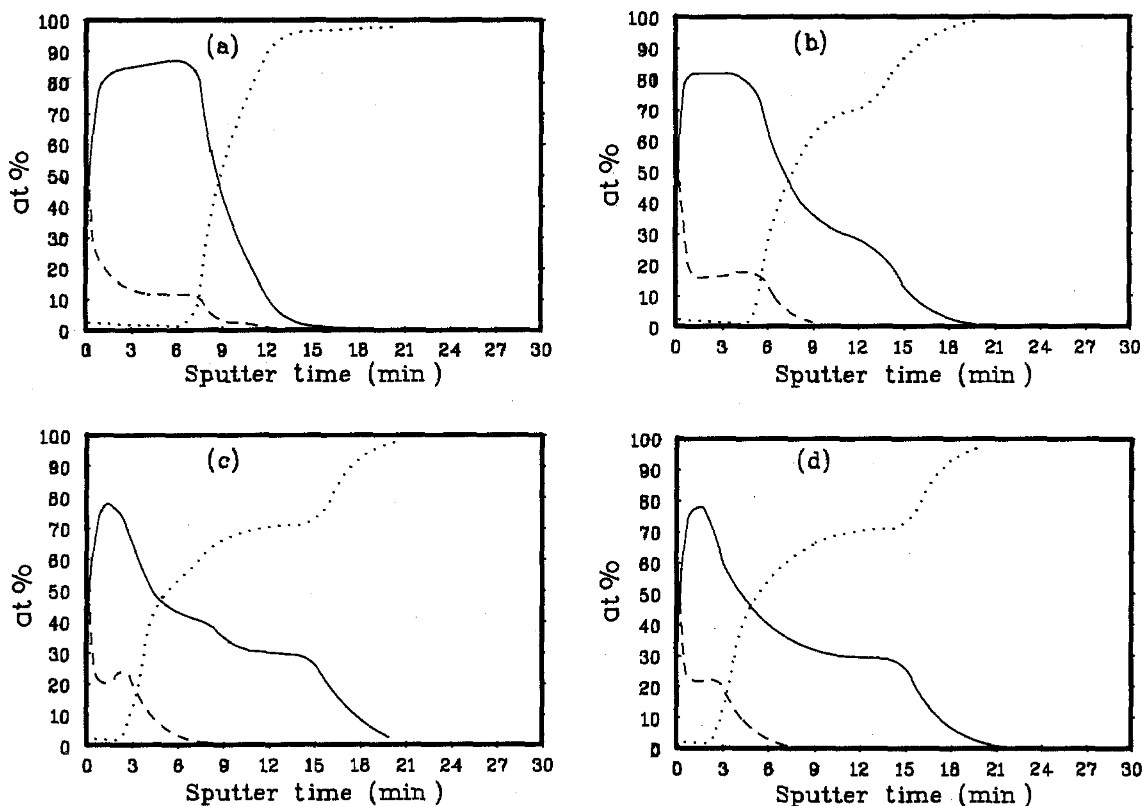

Figure 3 AES depth profiles of a 50 nm titanium film on (1 0 0)Si substate: (a) rapid thermal annealing at 600° C for 5 sec; (b) 600° C, 30 sec; (c) 600° C, 60 sec; (d) 600° C, 180 sec. (——) Titanium; (····) silicon; (– – –) oxygen.

AES. This snowplow effect associated with silicide growth results in the increase of oxygen concentration in the unreacted titanium layer. An interesting feature in Fig. 3 is that the oxygen profiles are changed according to the annealing time. Until 30 sec annealing, the oxygen in the unreacted titanium layer is distributed uniformly except near the surface, whereas the oxygen concentration in the unreacted titanium layer is gradually increased from 12 to 18 at % as silicide growth progresses. This uniform distribution of oxygen is attributed to the faster redistribution rate of oxygen in comparison with the silicide growth rate. On the other hand, the narrow oxygen peak in front of the Ti/silicide interface after 60 sec annealing at 600° C indicates that the oxygen segregated out of the silicide layer can not be redistributed as fast as the advancing silicide front moves into the unreacted titanium layer. Owing to this crossover in the oxygen and the silicon diffusion rates between 30 and 60 sec annealing, the oxygen is piled-up in front of the Ti/silicide interface. We attribute this crossover in the oxygen and the silicon diffusion rates to the increased oxygen concentration in the unreacted titanium layer. For further annealing after the exhibition of oxygen peak, the oxygen is redistributed uniformly again as shown in Fig. 3d. It may be related to the reduction of the segregation rate of oxygen, which results from the increased chemical potential of the piled-up oxygen, and to the reduced silicide growth rate. After the exhibition of the oxygen peak, the silicide growth is almost stopped even though there remains half of the deposited titanium film, about 25 nm, to be unreacted as shown in Figs 3c and d. In other words, no further silicide growth occurs after the oxygen is accumulated to approximately 20 at % in the unreacted titanium layer. This results in the early saturation of the sheet resistance before complete conversion of the deposited titanium film into silicide. Figure 4 shows the Auger depth profiles of the a-Si/Ti/(1 0 0)Si structured sample rapidly annealed at 600 and 700° C for 60 sec. The silicide formation occurs at both interfaces of a-Si/Ti and Ti/(1 0 0)Si. The silicide growth rate is faster at the a-Si/Ti interface than at the Ti/(1 0 0)Si interface as shown in Fig. 4a. Moreover, there is no change in the oxygen depth profiles before and after the heat treatment. Consequently, the sheet resistance of the a-Si/Ti/(1 0 0)Si structured sample continues to decrease without rapid increase near the onset of silicide formation as shown in Fig. 1b, and it reaches to lower saturated sheet resistance because of the complete conversion of the deposited titanium film into $TiSi_2$ as shown in Fig. 4b. No redistribution of oxygen during the heat treatment suggests that the oxygen at the surface of the a-Si forms a stable compound, SiO_2, with the a-Si. This native SiO_2 is not decomposed even at the annealing temperature ranging from 500 to 800° C. ESCA depth analysis is carried out to examine the chemical state of the oxygen in the titanium film of the Ti/(1 0 0)Si structured sample and in the a-Si film of the a-Si/Ti/(1 0 0)Si structured sample. In Fig. 5, the binding energy of 1s electron of oxygen is shown along with the film depth. For the Ti/(1 0 0)Si structured sample annealed at 600° C for 60 sec, the oxygen at the surface of the unreacted titanium layer favours the formation of titanium oxide, which is conformed by the $Ti2p_{3/2}$ peak at the binding energy of 458.5 eV. However the oxygen snowplowed back to the unreacted titanium layer tends to be atomic oxygen as a solute in the titanium film. This is evidenced by the shift of binding energy of the 1s electron of oxygen

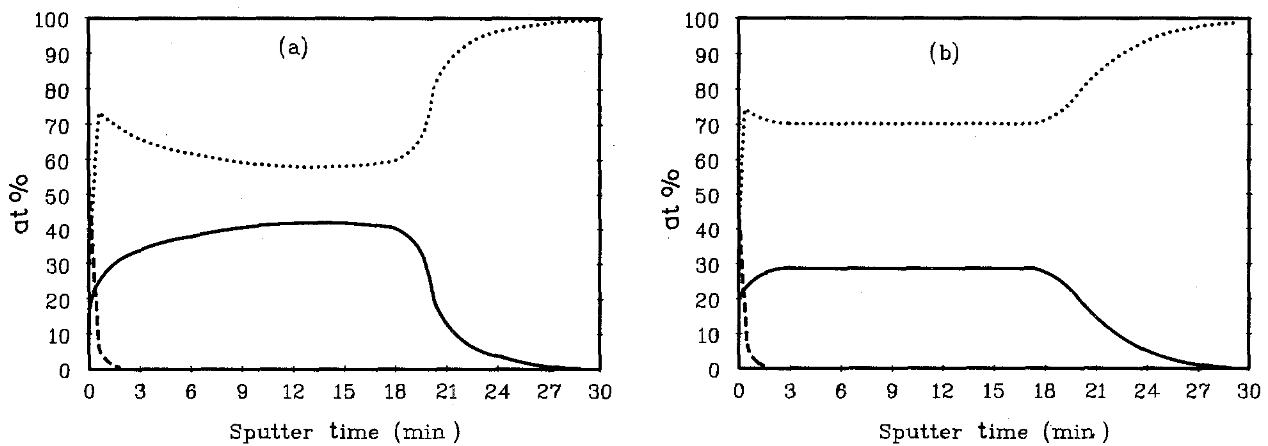

Figure 4 AES depth profiles of a 50 nm titanium film sandwiched between a silicon substrate and a 30 nm a-Si overlayer after rapid thermal annealing: (a) at 600° C, 60 sec; (b) at 700° C, 60 sec. (——) Titanium; (· · · ·) silicon; (– – –) oxygen.

from titanium oxide (530.6 eV) to oxygen atom (532.2 eV) as the film depth increases. This binding energy shift indicates that when the titanium film is exposed to air, it takes in oxygen and forms titanium oxide initially. During annealing the titanium oxide is decomposed into oxygen and titanium. The decomposed oxygen diffuses into the titanium film very rapidly and is snowplowed back to the surface as silicide growth progresses. For the a-Si/Ti/(1 0 0)Si structured sample annealed at 600° C for 60 sec, the binding energy of the 1s electron of oxygen, 533 eV, indicates that the oxygen forms SiO_2 with a-Si. Since this native SiO_2 is stable up to the experimental temperature, 800° C, the oxygen is not redistributed. Therefore, the a-Si film deposited on the titanium film protects the titanium film from oxygen impurity during annealing and is useful to complete the conversion of the deposited titanium film into silicide.

4. Summary

In this paper we have shown that the Ti/(1 0 0)Si structured sample and the a-Si/Ti/(1 0 0)Si structured sample exposed to air takes in oxygen at the surfaces. In case of the Ti/(1 0 0)Si structure, the native titanium oxide at the surface is decomposed and distributed uniformly throughout the titanium film during annealing. We found that the rapid increase of sheet resistance near the onset of silicide formation has a very close relation with the oxygen distribution in the titanium film. After the onset of silicide formation, the oxygen is expelled by the advancing silicide front and the sheet resistance is dominated by the lower resistivity silicide layer. Owing to the increased oxygen concentration in the unreacted titanium film, the silicide growth is almost stopped before the deposited titanium film is completely converted into silicide. In the case of the a-Si/Ti/(1 0 0)Si, the silicide begins to be formed at the a-Si/Ti and Ti/(1 0 0)Si interfaces simultaneously, whereas the oxygen is confined at the surface without redistribution during annealing. Since the redistribution of oxygen does not occur, the deposited titanium film is completely converted into silicide, and this leads to lower saturated sheet resistance. By depositing a-Si film on titanium film without breaking the vacuum, the unexpected influences of oxygen on the silicide formation were removed. The a-Si capping layer on the titanium film may also be useful in reducing the dopant redistribution during annealing.

References

1. M. E. ALPERIN, T. C. HOLLOWAY, R. A. HAKEN, C. D. GOSMEYER, R. V. KARNAUGH and W. D. PARMANTIE, *IEEE Trans. Electron Devices* **ED-32** (1985) 141.
2. E. S. BUMPS, H. D. KESSLER and M. HANSEN, *Trans. ASM* **45** (1953) 1008.
3. G. G. BENTINI, M. SERVIDORI, C. COHEN,

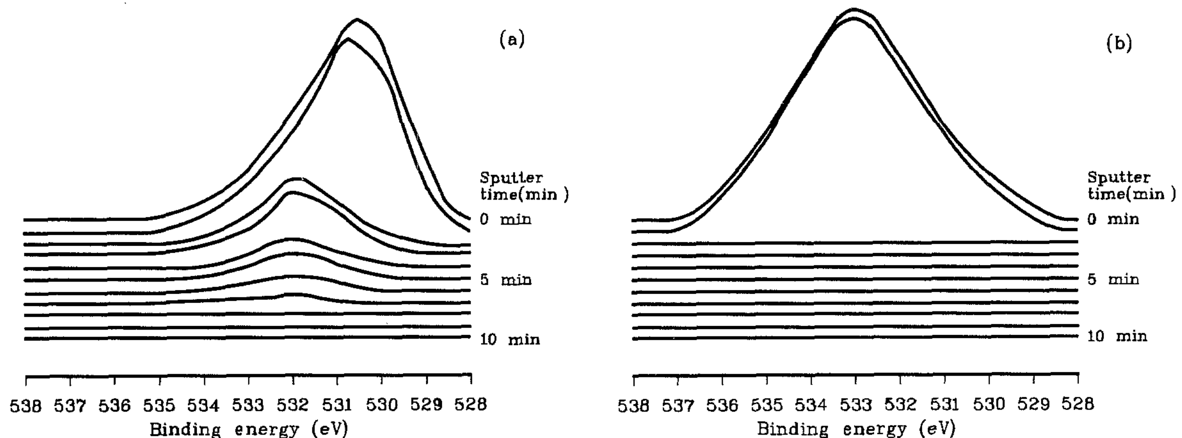

Figure 5 ESCA depth analysis of the oxygen after RTA at 600° C for 60 sec. (a) The binding energy of 1s electron of oxygen in the titanium film of the Ti/(1 0 0)Si structured sample, (b) the binding energy of 1s electron of oxygen in the a-Si film of the a-Si/Ti/(1 0 0)Si structured sample.

R. NIPOTI and A. V. DRIGO, *J. Appl. Phys.* **53** (1982) 1525.
4. P. MERCHANT and J. AMANO, *J. Vac. Sci. Technol.* **B2** (1984) 762.
5. C. A. MOORE, J. J. ROCCA, G. J. COLLINS, P. E. RUSSEL and J. D. GELLER, *Appl. Phys. Lett.* **45** (1984) 169.
6. R. PANTEL, D. LEVY, D. NICOLAS and J. P. PONPON, *J. Appl. Phys.* **62** (1987) 4319.
7. D. PRAMANIK, A. N. SAXENA, OWEN K. WU, G. G. PETERSON and M. TANIELIAN, *J. Vac. Sci. Technol.* **B2** (1984) 775.

Received 27 July 1988
and accepted 5 January 1989