ANODIC DISSOLUTION OF SILICON IN HYDROFLUORIC ACID

E.A.Efimov and I.G.Erusalimchik

The etching of silicon, for cleaning and shaping the surface, is of the greatest importance in semiconductor technology. The quality of the etching treatment and the condition of the silicon surface have a profound effect on the characteristics, stability, and reliability of the semiconductor.

The anodic behaviour of single-crystal silicon has already been investigated[1-3]. The anodic dissolution of silicon, like that of germanium, was shown to require the participation of holes; a saturation current of the order of 10^{-5} A cm^{-2} in 5% HF, due to insufficiency of holes, is observed in the polarisation curve of n-type silicon[3]. Flynn concluded[3], from the magnitude of the saturation current, that the holes needed for the anodic dissolution of silicon arise mainly from generation in the space-charge layer.

It has also been reported[1,2] that a thick, amorphous, high-resistivity film appears on the surface of p-type silicon during anodic dissolution in aqueous HF solutions. According to Turner, this film consists of various fluorosilicate compounds of divalent silicon which are unstable towards aqueous solutions and are oxidised by H^+ ions to quadrivalent silicon compounds. The film remains on the surface of the silicon anode up to a critical current density ($10^{-1}-10^{-2}$ A cm^{-2}) but decomposes at higher currents. The end product of the anodic dissolution of silicon in HF is fluorosilicic acid.

EXPERIMENTAL

We have applied polarisation and capacity measurements to the study of the anodic dissolution of silicon, both n- and p-type, of resistivity around 10 ohm cm, in 2.5 N HF at 20°. All the silicon samples had a (111) crystallographic orientation and a minority-carrier lifetime of 30–40 μsec. The apparatus and every part of the electrolytic cell were made of Teflon. Potentials were measured against a saturated calomel half-cell and converted to the hydrogen scale. Ohmic contacts to the silicon were prepared by rhodium plating.

Before each experiment the surface of the silicon anode was treated with a 1 : 2 mixture of HF and HNO_3, followed by 42% HF. Potential–time curves were displayed on an oscilloscope of type ENO-1. Capacity measurements were carried out as previously described[4].

Both p- and n-type silicon will dissolve anodically in aqueous solutions of hydrofluoric acid and of fluorides. Fig. 1 gives anodic polarisation curves for p- and n-type silicon over the range of current densities $10^{-6}-10^{-2}$ A cm^{-2}. Curve *1*, typical of the anodic behaviour of n-type silicon, has a clearly defined limiting current which is lacking in the curve for p-type silicon (curve *2*). The $\varphi - \log I$ relationship for the latter electrode is linear over the range of current densities $10^{-6}-5\times10^{-3}$ A cm^{-2}, with a slope $b \simeq 0.1$ V.

It can be seen from Fig. 1 that the anodic behaviour of p- and n-type silicon is identical at potentials lower than 0.1 V. At more positive potentials the electrode process depends on the conductivity type of the silicon.

The anodic dissolution of silicon, like that of germanium, should depend on the concentration of holes at the semiconductor/electrolyte interface. The limiting current, observed with n-type silicon at potentials higher than 0.1 V, is in fact a saturation current of holes, which are consumed by the electrochemical reaction. In p-type silicon the holes are the majority carriers, their concentration is large, and no hole saturation current is observed (curve *2*).

The magnitude of the saturation current for n-type silicon (10^{-4} A cm^{-2}) confirms Flynn's suggestion[3] that the holes consumed by the anodic reaction are effectively generated in the space-charge layer rather than in the bulk of the semiconductor. Indeed, calculations of the saturation current indicate that the limiting diffusion current would be as small as $10^{-7}-10^{-8}$ A cm^{-2} if holes had to be supplied to the electrode surface from the bulk of the semiconductor. In practice, saturation is observed at significantly higher current densities ($\sim 10^{-4}$ A cm^{-2}).

The curves of Fig. 1 thus show that the anodic dissolution of silicon, in common with that of germanium, is controlled by the number of holes at the semiconductor/electrolyte boundary. It follows that any process able to increase the hole density in the near-surface layer (hole injection, illumination of the electrode, temperature rise, etc.) should decrease the polarisation of an n-type silicon electrode.

Gerischer and Beck[5] have shown that oxidising agents, added to the electrolyte, may under certain conditions be reduced by capturing electrons from the valence band of germanium. The resulting holes favour the anodic dissolution process. An analogous behaviour can also be observed with silicon. The addition of $K_3Fe(CN)_6$ to the solution appreciably increases the saturation current of n-type silicon (curve *3* of Fig. 1).

Oxide films of different composition can be visually observed on the surface of n- and p-type silicon electrodes which have undergone anodic dissolution. On p-type silicon the film is dark in colour, and is hardly attacked by concentrated HF, but dissolves easily in cold KOH solution

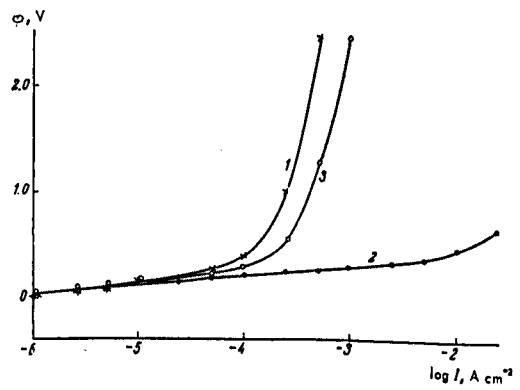

Fig. 1. Anodic polarisation in the dissolution of silicon: 1) n-type silicon in 2.5 N HF; 2) p-type silicon in 2.5 N HF; 3) n-type silicon in 2.5 N HF + 0.05 N $K_3Fe(CN)_6$.

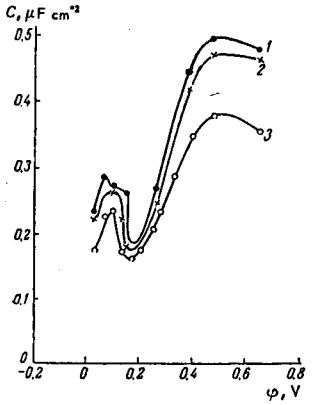

Fig. 2. Differential capacity of p-type silicon in 2.5 N HF at different frequencies, c/s: 1) 200; 2) 1000; 3) 10 000.

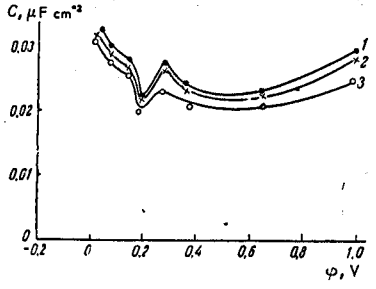

Fig. 3. Differential capacity of n-type silicon in 2.5 N HF at different frequencies, c/s: 1) 200; 2) 1000; 3) 10 000.

with vigorous evolution of hydrogen. The film on n-type material is much thinner, practically unaffected by KOH, but readily soluble in concentrated HF. Obviously, bivalent silicon compounds must predominate in the film on p-type silicon whilst quadrivalent compounds predominate in the other film. The presence of oxide films on the silicon surface may also be demonstrated oscillographically. Films of this type must radically influence the kinetics of anodic dissolution.

The state of the silicon-electrode surface was studied by double-layer capacity measurements at various positive potentials and also by observing the change in potential with time when the polarising current was switched from cathodic to anodic.

Figs. 2 and 3 show differential capacity curves for p- and n-type silicon anodes in 2.5 N HF, measured at frequencies of 200, 1000, and 10 000 c/s. These curves are

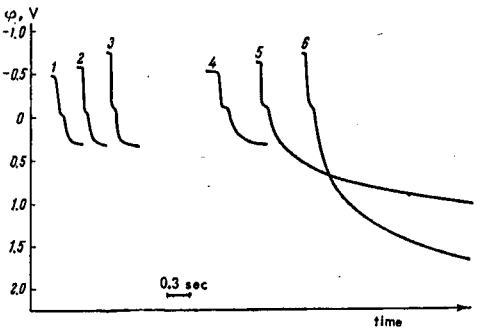

Fig. 4. Electrode potential–time curves on switching the current from cathodic to anodic: 1) p-type silicon, I = $= 10^{-4}$ A cm^{-2}; 2) p-type silicon, $I = 2 \times 10^{-4}$ A cm^{-2}; 3) p-type silicon, $I = 5 \times 10^{-4}$ A cm^{-2}; 4) n-type silicon, I = $= 10^{-4}$ A cm^{-2}; 5) n-type silicon, $I = 2 \times 10^{-4}$ A cm^{-2}; 6) n-type silicon, $I = 5 \times 10^{-4}$ A cm^{-2}.

reminiscent of the $c-\varphi$ curves for the germanium anode[4], but the capacity values are significantly lower. The capacity is a sensitive function of the conductivity type for both the silicon and the germanium electrode. For p-type silicon (Fig. 2) it is about an order of magnitude higher than for n-type (Fig. 3). This effect clearly arises from differences in the depth of the depletion layer. n-Type silicon has a thicker layer in which the current carriers are depleted than has p-type silicon. An increase in the thickness of the depletion layer may be likened to an increase in the separation of the plates of a condenser: the capacity of a p-type silicon anode will therefore be higher than that for n-type silicon.

The lower capacity values observed on silicon (as compared with those on germanium) must likewise be due to the thicker depletion layer and the lower equilibrium carrier density of silicon, and also to the higher degree of oxidation of the silicon anode.

The $c-\varphi$ curves for p-type silicon, measured at three frequencies, all go through a sharp minimum at a potential of about 0.2 V relative to the normal hydrogen electrode. The capacity reaches a maximum at $\varphi \simeq 0.5$ V and then begins to fall off. The same phenomenon is shown by the germanium electrode[4]. With n-type silicon the minimum at 0.2 V is retained but no steep increase in capacity is observed on further increasing the potential.

Fig. 4 shows some oscillographic displays of the potential on switching the current from the cathodic to the anodic direction. The curves for p-type silicon (curves $1-3$) have two arrests, at ~ 0 and ~ 0.25 V. The length of the first arrest increases with duration of the preliminary cathodic polarisation, but not the length of the second arrest. The arrest at ~ 0 V is connected with the removal of the hydrogen adsorbed on the silicon surface; the other arrest arises from the adsorption of oxygen. The region between the two arrests corresponds to charging of the double layer. The potential of the second arrest is independent of the current density used.

The electrochemical adsorption of oxygen by a silicon surface, leading to a decrease in differential capacity, may be assumed to set in at potentials somewhat below 0.2 V. The steep rise in the capacity curve for n-type

silicon (Fig. 2) above 0.2 V can be ascribed to a significant increase in the rate of electrochemical dissolution of the silicon, which introduces a pseudo-capacity. This view is confirmed by observations of a certain amount of capacity dispersion and by the absence of any such rise in the curve for n-type silicon (Fig.3), whose rate of reaction is sharply retarded by lack of holes at potentials higher than 0.1 V. The fall in capacity at 0.4–0.5 V (Fig. 3) or the decrease in its rate of growth (Fig. 2) are obviously due to the nucleation of a new phase of oxide, a conclusion supported, as stated above, by the visual appearance of the surface. The $\varphi - \log I$ curve for p-type silicon begins to depart from linearity at ~0.4 V, again confirming that a distinct phase of oxide is present on the silicon surface under these conditions.

The existence of oxides of different chemical composition on p- and n-electrodes is illustrated in Fig. 4. The more extended time of growth of anodic potential (curves *4–6*) is characteristic of n-type silicon. It is due to the fact that an n-type silicon anode can attain a high potential, as a result of hole depletion, and this leads to the formation of an oxide phase at current densities which only cause electrochemical adsorption of oxygen on p-type silicon.

The primary act of the anodic dissolution process is obviously the electrochemical oxidation of the silicon--electrode surface; the next stage is the transfer into the solution of the resulting fluorosilicate surface complexes; this latter stage is limited by the number of holes at the semiconductor surface in contact with the electrolyte.

When insufficient holes are present, as is the case with n-type silicon, the transfer of surface species into the solution is difficult, but the electrochemical oxidation of the surface is not retarded. This is probably the reason why the oxide phase on n-type silicon contains predominantly quadrivalent silicon compounds, whereas on p-type silicon divalent compounds predominate.

SUMMARY

1. The anodic dissolution of p- and n-type silicon in a 2.5 N solution of hydrofluoric acid has been studied by polarisation and capacity measurements. The kinetics of the process are found to be limited by the generation of holes in the space-charge layer of the semiconductor surface.
2. The differential capacity of the silicon electrode is found to be significantly lower than that of germanium, and furthermore the capacity of n-type silicon is lower than that of p-type on account of the former's thicker space--charge layer.
3. It is shown that chemically different surface oxides appear on p- and n-type silicon electrodes subjected to the same current density. Their formation potentials are discussed.

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2. Turner, J. Electrochem. Soc., 105, 402 (1958).
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INFLAMMATION LIMITS OF BUTANE WITH OXYGEN AND THE EFFECT OF SURFACE

V. A. Poluektov, S. Ya. Pshezhetskii, and V. M. Cherednichenko

In the inflammation of hydrocarbons with oxygen a second pressure limit has been observed with methane and ethane[1,2]; with higher hydrocarbons a second limit has been found only on oxidation with air[2a]. Some results[3-5] suggest that the second limit for these hydrocarbons was connected with the after-burning of CO. The inflammation "peninsula" of methane and ethane lies approximately in the same region as that of CO. A second limit was not observed when a surface, which catalysed the after-burning of CO, was introduced[3]. If the appearance of the second limit was connected with the after-burning of CO, it should also have been observed with other methane homologues.

This paper deals with the inflammation limits of butane with oxygen and the effect of surface. A second limit is also observed with butane. The inflammation "peninsula" of butane lies at approximately the same pressure as, but at a somewhat lower temperature than, for methane and ethane.

EXPERIMENTAL

The oxygen, obtained by the electrolysis of water, was carefully purified and dried. The butane was purified by passing through a column of sulphuric acid and dried. From distillation in a Podbielniak column the butane contained 0.2% of ethane and 0.1% of propane.

The cylindrical reaction vessel (diameter 2.9 cm, length 17.0 cm) was made from quartz and the surface area was varied by filling the vessel with quartz tubes 1.5–2.0 cm long, 0.3–0.4 cm in internal diameter, and 0.1 cm thick. Before experiment the butane and oxygen were mixed in stoichiometric proportions, to an accuracy of ±0.5 mm Hg. The temperature of the walls of the reaction vessel was maintained constant within ±0.5° and the induction period was measured with an accuracy of ±0.1 sec.

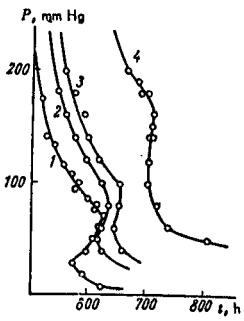

Fig. 1. Inflammation limits of a stoichiometric mixture of butane and oxygen: 1) in the empty vessel; 2) packing surface area 302 cm^2; 3) packing surface area 574 cm^2; 4) packing surface area 864 cm^2.