SURFACE STATE OF ANODICALLY POLARISED SILICON IN DILUTE HYDROFLUORIC ACID

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The state of a silicon surface during anodic dissolution at high current densities (10^{-2}–10^{-1} A cm^{-2}) has been investigated by Turner[1]. The processes occurring on the surface at current densities below 10^{-2} A cm^{-2} have not been investigated.

A study has now been made, based on measurements of capacitance and on charging curves, of the surface state of p- and n-type silicon after anodic polarisation in 2.5 N HF at current densities of 10^{-5}–10^{-2} A cm^{-2}.

EXPERIMENTAL

Cathodic charging curves were obtained at $I_c = 10^{-3}$ A × × cm^{-2} after anodic polarisation of the electrode at various current densities for 20–120 sec, the technique having been described in Ref.2. All the investigations were carried out at 20° on single crystals of p- and n-type silicon having a resistivity of 10 ohm cm and a carrier lifetime of 30–40 μsec, oriented in the (111) direction. Before each experiment the electrodes were treated with a mixture of HF + HNO_3 (1 : 2) and then with 42% HF.

Figs.1 and 2 show charging curves for p- and n-type silicon obtained after 20 sec anodic polarisation at various current densities. Identical curves were obtained when the period of anodic polarisation was increased to 120 sec. The character of the change in potential with the quantity of electricity passed is seen to be different for the two types of silicon. While the curves for n-type silicon (Fig.2) show a slight arrest in the growth of potential, those for the p-type (Fig.1) show no such arrest. On the contrary, the potential immediately reaches a definite maximum when the cathodic current is switched on, after which it drops. This type of charging curve indicates that the anodic oxidation of silicon is irreversible, the oxide film which is formed remaining almost unreduced on

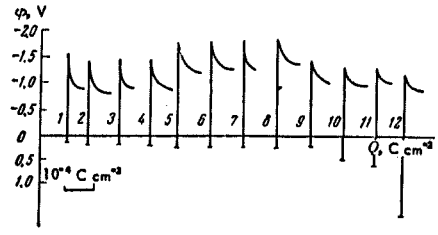

Fig.1. Cathodic charging curves obtained with p-type silicon after anodic polarisation at various potentials, V: 1) 0.100; 2) 0.145; 3) 0.175; 4) 0.195; 5) 0.230; 6) 0.250; 7) 0.275; 8) 0.325; 9) 0.375; 10) 0.475; 11) 0.650; 12) 1.50.

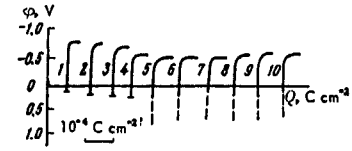

Fig.2. Cathodic charging curves obtained with n-type silicon after anodic polarisation at various potentials, V: 1) 0.140; 2) 0.170; 3) 0.265; 4) 0.360; 5) 1.000; 6) 2.750; curves obtained at various current densities, A cm^{-2}; 7) 10^{-3}; 8) 2.5×10^{-3}; 9) 5×10^{-3}; 10) 10^{-2}.

cathodic polarisation. The slight arrest (~5×10^{-5} C cm^{-2}) observed in Fig.2 is obviously associated with the removal from the surface of only a very small quantity (approximately equal to one-eighth of a monolayer) of surface oxygen.

Such an arrest is absent with p-type silicon. The peaks on the curves in Fig.1 are probably due to saturation of the silicon surface with hydrogen during the cathodic polarisation, as occurs with germanium. By penetrating the crystal lattice of the silicon, hydrogen increases the number of centres for the generation of current carriers, both by the formation of additional levels and by the development of lattice defects. The result is to increase the surface conductance of p-type silicon and decrease the additional potential difference in the surface layer of the semiconductor which has been depleted in current carriers. The potential peak which is produced may mask the slight arrest which should be observed also on the curves for p-type silicon.

During the anodic dissolution of silicon, oxides are formed on its surface, which can even be detected visually. Under the microscope, brown oxide spots can be observed on the surface of p-type silicon after anodic polarisation at $I > 5 \times 10^{-4}$ A cm^{-2}. The colour of the surface oxide becomes pale grey.

The curves in Fig.1 show that the potential of hydrogen evolution depends on the preliminary polarisation of the electrode. Thus after anodic polarisation at current densities in the range 10^{-5}–10^{-4} A cm^{-2} (φ = 0.10–0.20 V) the potential for hydrogen evolution at $I_c = 10^{-3}$ A cm^{-2} is ~ -0.7 V.

When the preliminary anodic polarisation is increased above 0.2 V, the potential for hydrogen evolution jumps to ~ -1.4 V, this value being maintained over the range $I_c = 2.5 \times 10^{-4}$–2.5×10^{-3} A cm^{-2} (φ = 0.23–0.32 V). With further increase in the preliminary anodic polarisation ($\varphi \geq 0.37$ V) the potential of hydrogen evolution falls to about -0.8 V. This phenomenon is probably due to the formation on p-type silicon at φ = 0.2 V of a definite surface oxide for which the hydrogen overpotential is higher. This oxide changes its structure at ~0.33–0.37 V. The new oxide which is formed differs in colour and has a lower hydrogen overpotential.

The formation of surface oxides on p-type silicon at potentials of 0.20 and 0.33–0.37 V is confirmed by measurements of the impedance of the electrode. Fig.3 shows a minimum in the capacitance curve and a maximum in the resistance curve at $\varphi \simeq 0.20$ V. At ~0.4 V the capacitance approaches its maximum value, while the resistance becomes constant.

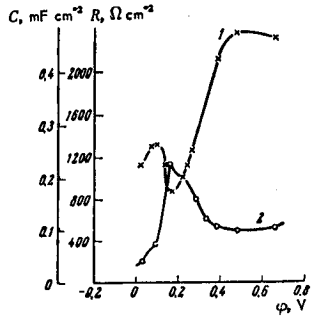

Fig. 3. Curves for p-type silicon at a frequency of 1000 c/s:
1) capacitance; 2) resistance.

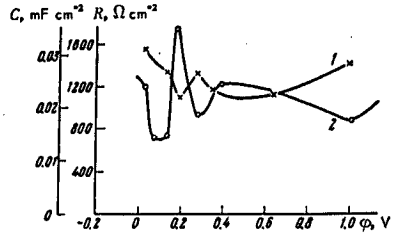

Fig. 4. Curves for n-type silicon at a frequency of 1000 c/s:
1) capacitance; 2) resistance.

With n-type silicon it is impossible, on the basis of the available experimental data, to determine with equal clarity the potentials at which surface oxides are formed. In this case too, however, the curves in Fig. 4 show a slight minimum in the capacitance and a maximum in the resistance of the electrode at $\varphi \simeq 0.2$ V. After anodic polarisation at $\varphi \simeq 0.36$ V, there is a slight fall in the hydrogen overpotential (Fig. 2). It should be noted that a given range of anodic potentials corresponds to a considerably narrower range of current densities with n-type than with p-type silicon. This makes it difficult to determine accurately the potential at which oxides are formed on n-type silicon. Another result is that oxides differing in composition can be formed on the surface of the two types of silicon at identical anodic current densities.

SUMMARY

1. An investigation has been made, by means of charging curves and capacitance measurements, of the surface state of silicon which has been polarised anodically in 2.5 N hydrofluoric acid over the range of current densities 10^{-6}–10^{-2} A cm^{-2}.
2. Oxides are formed on the surface at ~0.2 and 0.3–0.4 V during the anodic dissolution of silicon. These compounds differ from one another in structure and have different hydrogen overpotentials.

1. D.R. Turner, J. Electrochem. Soc., 105, 402 (1958).
2. E.A. Efimov and I.G. Erusalimchik, Dokl. Akad. Nauk SSSR, 134, 1387 (1960).

Moscow Received 19th July 1960

SURFACE TENSION AT THE LIQUID–GAS INTERFACE UNDER HIGH PRESSURES

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With the extensive development of high-pressure chemical and physicochemical processes the need arises for information on surface tension, especially at the liquid–gas interface. Many accurate determinations have been made of surface tension at the liquid–gas interface under atmospheric pressure and at various temperatures, but much less work has been done at high pressures. The same experimental techniques are used at high pressures as at atmospheric pressure, the most suitable being the capillary-rise method, the maximum-bubble-pressure method and the drop-weight method. The theoretical basis of these methods is given, together with references, in the standard textbooks[1–3], while information on the design of apparatus is given by Tsiklis[4].

EXPERIMENTAL

In this work we used the capillary-rise method with visual observation of the difference in heights in two connected capillaries of different diameters; this difference lay between 8 and 15 mm. To determine surface tension by the single-capillary method, Laplace's formula is used:

$$\sigma = \frac{rh(\gamma_1 - \gamma_2)g}{2\cos\theta}, \quad (1)$$

where σ is the surface tension, r the capillary radius, h the height to which the liquid rises, γ_1 the specific gravity of the liquid, γ_2 the specific gravity of the gas phase, θ the wetting angle, and g the acceleration due to gravity. However, it is more convenient to use a double capillary, since this offers the possibility of working with a single drop of liquid, and a null surface is clearly visible. For a capillary U-tube, Laplace's formula becomes:

$$\sigma = \frac{\Delta h(\gamma_1 - \gamma_2)g}{2\cos\theta} \cdot \frac{r_2 r_1}{r_2 - r_1}, \quad (2)$$

where $\Delta h = h_1 - h_2$ is the difference between the heights in the narrow and the wide capillaries, and r_1 and r_2 are the corresponding capillary radii. Published data[5] show that for the liquids we examined and glass capillaries the wetting angle is zero, so that $\cos\theta = 1$. Hence, combining all the constants of Eqn. (2), we get

$$\sigma = K\Delta h\Delta\gamma, \quad (3)$$

where

$$K = \frac{r_2 r_1 g}{(r_2 - r_1)2\cos\theta}. \quad (4)$$