

with an increase in weight of $25 \mu\text{g cm}^{-2}$ after 10 h. After oxidation of silicon under anodic conditions, the surface conduction changed from *p*-type to *n*-type.

For comparison with the data obtained by weighing the specimens, the results of optical measurements of the thickness of the oxide film on silicon oxidised under anodic conditions are also given. At a pressure of 1.2 mm Hg, a voltage between the electrodes of 300–330 V, and a discharge current density of 2 mA cm^{-2} the film was 60–70 Å thick and no iridescence had appeared on the specimen. Further oxidation at 0.84 mm Hg and 360–370 V gave a film thickness of 300–310 Å after 6 h. Results obtained by the two methods are in satisfactory agreement.

Curves 5 and 6 in Fig. 3 represent the oxidation of *n*-type silicon. Since a higher voltage is established at specimens of *n*-type silicon during oxidation, the intensity of oxidation at the given pressure (0.8 mm Hg) is greater in spite of the lower current density (curves 2 and 4). After silicon had been oxidised under anodic conditions, its surface conduction changed from *n*-type to *p*-type. In none of the experiments did the temperature of the specimen exceed 100° .

Behaviour of Germanium Connected in the Circuit as Cathode

A germanium anode which has been oxidised in the discharge until its weight has increased by $34 \mu\text{g cm}^{-2}$ exhibits a continuous loss in weight when made the cathode. The oxide film vaporises in the course of 2 h (at 580–590 V and 0.4 mA cm^{-2}).

In order to study the effect of an oxide film formed in a glow discharge on the working of planar silicon triodes, bench tests were made on triodes which had been oxidised by the author and on unoxidised specimens from the factory. An oxide film formed on the surface of the element in the discharge gives complete protection from the action of moisture and other corrosive agents. Although the current amplification factor is considerably lowered, other parameters of the instrument are not impaired. These changes are evidently due to the formation of electron traps arising from interaction of the surface of the element with oxygen, and also to the development of structural defects after removal of ions from the lattice under the influence of the electric field and the growth of the oxide film.

SUMMARY

The behaviour of germanium and silicon when used as glow-discharge electrodes in oxygen has been investigated. Employment of these elements as anodes results in the appearance of oxide layers on their surfaces. Cathodic treatment of the oxidised material removes the oxides from its surface.

A glow discharge in oxygen greatly affects the state of a germanium or silicon surface, and their electrical characteristics are also changed:

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Received 22nd July 1960

ELECTROCHEMICAL HYDROGEN EVOLUTION AT A SINGLE CRYSTAL OF SILICON IN DILUTE HYDROFLUORIC ACID

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A study has been made of the evolution of hydrogen at *p*- and *n*-type silicon cathodes in 2.5 *N* aqueous hydrofluoric acid. The choice of electrolyte was governed by the fact that this acid forms the main component of all solutions and etching agents employed in semiconductor technology for the treatment of silicon and of *p*-*n* junctions in silicon devices.

EXPERIMENTAL

Rapid and slow polarisation measurements, current-growth oscillograms, and charging curves were used in studying the mechanism of the electrochemical reaction. All parts of the electrolytic cell were made of Teflon. Experiments were carried out in previously redistilled 2.5 *N* HF at room temperature. The cathode material was single-crystal *p*- and *n*-type silicon having a resistivity of 10 ohm cm and a lifetime of the minority current carriers of 40 μsec . The crystallographic orientation was (111). All polarisation measurements were preceded by the passage of carefully purified hydrogen through the cathodic compartment of the electrolytic cell for 5 h. The slow

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recording of polarisation curves was preceded by preliminary cathodic polarisation at 10^{-2} A cm $^{-2}$ for 1 h, after which the hydrogen overpotential was measured at current densities between 2.5×10^{-3} and 5×10^{-2} A cm $^{-2}$.

Rapid polarisation measurements were made by means of an ENO-1 oscilloscope and a special sawtooth-pulse generator, which allowed the period of application of voltage to the cell to be varied from 30 to 10^{-4} sec. The sawtooth oscillator and the timebase generator of the oscilloscope were started synchronously by means of a special device.

Charging curves were obtained after preliminary cathodic polarisation of the electrode at various potentials for a fixed time, after which the anodic charging curve was recorded at a current $I_a = 5 \times 10^{-3}$ A cm $^{-2}$.

DISCUSSION

Fig. 1 shows η -log I polarisation curves obtained for n - and p -type silicon by the slow method with preliminary polarisation. In appearance they greatly resemble the analogous curves obtained earlier in 2 N H $_2$ SO $_4$.¹ It is seen that the potential increases sharply at current densities of 10^{-3} and 10^{-2} A cm $^{-2}$ with p - and n -type silicon respectively. At potentials less negative than -0.7 V the hydrogen overpotential of the two types of silicon is the same and is represented by the Tafel equation with $b \approx 0.17$ V. As has been shown previously¹, the divergence between the curves for the two types of silicon is not due to the presence of a limiting diffusion current of electrons in the p -type silicon, but is caused by the voltage drop in the depleted layer of the semiconductor at the boundary with the electrolyte, which is included in the measured value of the overpotential.

Later a similar view was expressed by Paleolog *et al.*²

With silicon, as with germanium³, the evolution of hydrogen is greatly dependent on the extent of previous saturation of the electrode surface with hydrogen. Fig. 2 shows polarisation curves obtained over periods of 20 and 0.4 sec. In the latter case the potential of the p -type silicon electrode is appreciably higher, for example by 0.35 V at 2.5×10^{-3} A cm $^{-2}$, whereas the potential of n -type silicon remains unchanged. A limiting electron diffusion current is absent also from the curves in Fig. 2. The mutual approach of the curves as the period of measurement is diminished [?(Ed. of Translation)] can be explained

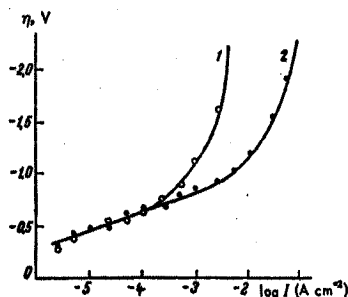


Fig. 1. Cathodic polarisation curves obtained in 2.5 N HF after preliminary polarisation: 1) p -type silicon; 2) n -type silicon.

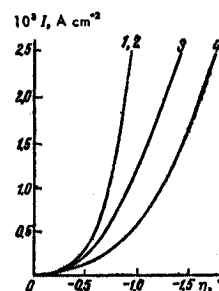


Fig. 2. Cathodic polarisation curves obtained in 2.5 N HF by the rapid method for different types of silicon with different periods for recording the curve:

- 1) n -type, 20 sec; 2) n -type, 0.4 sec; 3) p -type, 20 sec; 4) p -type, 0.4 sec.

by saturation of the electrode with hydrogen in the course of the electrochemical reaction. By being adsorbed on the silicon surface or penetrating inside the crystal lattice, the hydrogen creates new impurity levels and increases the number of centres for the recombination and generation of current carriers. This in turn increases the conductance of the surface layer of p -type silicon at the electrolyte boundary and thereby diminishes the additional potential drop observed with a surface which has not been saturated with hydrogen.

Previous cathodic treatment of the surface does not completely eliminate the difference in potential between n - and p -type electrodes, as occurs with germanium³. This is apparently due to the fact that the new levels produced by the hydrogen which penetrated into the electrode do not completely bridge the forbidden gap of the silicon.

Fig. 3 shows oscillograms obtained when the current is switched on at cathodes of p - and n -type silicon. These electrodes had first been subjected to very slight and brief anodic polarisation (at 10^{-5} A cm $^{-2}$) to remove adsorbed hydrogen, after which the cathodic current was switched on. At $I_c = 10^{-4}$ A cm $^{-2}$ the curves for the two types of silicon are identical. At $I_c = 10^{-3}$ A cm $^{-2}$ a sharp peak is observed on the p -type curve, reaching up to 2 V in height. Such peaks occur only with currents $\geq 2.5 \times 10^{-4}$ A cm $^{-2}$, i.e. over the range within which the η -log I curves for the two

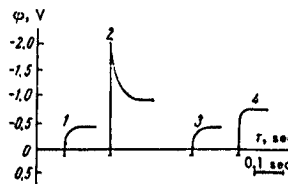


Fig. 3. Oscillograms obtained on switching on the current at p - and n -type silicon cathodes at different current densities (A cm $^{-2}$):

- 1) p -type, 10^{-4} ; 2) p -type, 10^{-3} ; 3) n -type, 10^{-4} ; 4) n -type, 10^{-3} .

types of silicon diverge. The existence of such a peak shows that even a very small quantity of adsorbed hydrogen causes the production of fresh current carriers, and thereby decreases the ohmic potential drop in the surface layer of *p*-type silicon.

In order to investigate the surface state of the silicon cathode during hydrogen evolution, anodic charging curves were obtained after preliminary cathodic polarisation at current densities of 10^{-5} – 10^{-2} A cm $^{-2}$. Fig. 4 shows such curves for *n*- and *p*-type silicon after cathodic treatment for 120 sec. Beginning at $I_c = 5 \times 10^{-5}$ A cm $^{-2}$ (polarisation potential -0.5 V) these curves show a well defined horizontal arrest in the potential at $\varphi_c \approx -0.3$ V on the normal hydrogen scale.

With *n*-type silicon the length of this plateau first increases with rise in potential and then remains approximately constant at $\sim 10^{-4}$ C cm $^{-2}$. With *p*-type silicon the arrest is somewhat greater (~ 1.7 – 2.7×10^{-4} C cm $^{-2}$) and is less definite. The existence of an arrest is due to the formation of some surface compound of silicon. Since it occurs only after previous cathodic polarisation at potentials more negative than -0.5 V, and is eliminated only at -0.3 V, its existence cannot be assumed to be due solely to the deposition and removal of atomic hydrogen without the formation of any stable chemical bond between the latter and the silicon atoms. In our opinion a compound similar to silicon hydride may be formed on the surface of a silicon cathode. An arrest of $(1-2) \times 10^{-4}$ C cm $^{-2}$ corresponds to 0.5–1 monolayer of hydrogen atoms. Decrease in the period of preliminary cathodic polarisation somewhat shortens the arrest: e.g. with *n*-type silicon it is 4×10^{-5} C cm $^{-2}$ after polarisation at 10^{-2} A cm $^{-2}$ for 20 sec.

Thus the curves in Fig. 4 indicate that hydrides are formed at the surface of *p*- and *n*-type silicon on cathodic polarisation at $\varphi_c \leq -0.5$ V. They cover a considerable proportion of the electrode surface, and therefore it is highly probable that the evolution of hydrogen on silicon passes through a stage in which such hydrides are formed.

Since valence electrons are always involved in a chemical bond, it is reasonable to postulate that electrons from the valence band are necessary for the formation of the chemical bond with the hydrogen atoms adsorbed on the silicon surface, regardless of the type of conduction of the semiconductor. Therefore hydride formation on *p*-type silicon should not be limited by the concentration of free electrons in the surface layer, and the reaction

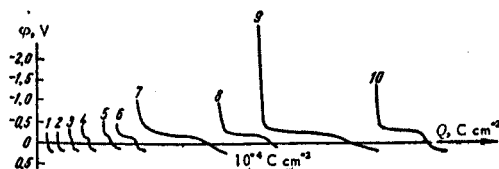


Fig. 4. Anodic charging curves obtained for *p*- and *n*-type silicon after preliminary polarisation at different cathodic current densities (in A cm $^{-2}$) for 120 sec:

- 1) *p*-type, 10^{-5} ; 2) *n*-type, 10^{-5} ; 3) *p*-type, 5×10^{-5} ;
- 4) *n*-type, 5×10^{-5} ; 5) *p*-type, 10^{-4} ; 6) *n*-type, 10^{-4} ;
- 7) *p*-type, 10^{-3} ; 8) *n*-type, 10^{-3} ; 9) *p*-type, 10^{-2} ;
- 10) *n*-type, 10^{-2} .

should take place at the same rate on *p*- and *n*-type silicon, with possible subsequent electrochemical desorption of hydrogen:



Electrons from the vacant and valence bands can take part in reaction (2), participation of a conduction electron being energetically the most favourable. In other words, reaction (2) takes place at a greater rate on *n*-type silicon. If reaction (1) takes place at the same rate on silicon having the two types of conduction, while reaction (2) is the slower of the two reactions, a greater quantity of chemically combined hydrogen should accumulate on the surface of *p*-type silicon.

This hypothesis is supported by the data illustrated in Fig. 4, from which it can be seen that the length of the arrests on the anodic charging curves for *p*-type silicon is greater if the preliminary cathodic polarisation has been carried out at potentials more negative than -0.7 V. It is at this potential that the η -log *I* curves for *p*- and *n*-type silicon diverge (Fig. 1).

The increased length of the hydrogen arrest for *p*-type compared with *n*-type silicon can also have a different explanation. Since the electronegativity of hydrogen is greater than that of silicon⁴, hydrogen adsorbed on the surface will form dipoles with their negative ends pointing outwards. A negative surface charge is then obtained on an *n*-type semiconductor, and this can be partly or completely balanced by the positive space charge in the surface barrier. An increase in adsorption will raise the barrier and limit further adsorption of hydrogen on *n*-type silicon. On *p*-type silicon each adsorbed ion will produce a vacant hole, able to take part in conduction. With this type of silicon the positive end of the dipole formed on the adsorption of hydrogen is a hole, not an ionised donor atom as in *n*-type silicon. Therefore the dipoles on *p*-type silicon do not extend inside the semiconductor, and their force fields are concentrated in a small volume. This makes it possible for fresh dipoles to be formed on the surface, i.e. for more hydrogen to be adsorbed.

In conclusion we express our gratitude to A. L. Zakharov for discussions of the results of the present work.

SUMMARY

1. The electrochemical evolution of hydrogen at *p*- and *n*-type silicon in 2.5 N HF has been studied at current densities between 2.5×10^{-6} and 5×10^{-2} A cm $^{-2}$.
2. The kinetics of the electrochemical reaction are affected by saturation of the silicon electrode with hydrogen in the course of cathodic polarisation.
3. On the basis of the anodic charging curves, it is suggested that a surface chemical compound of silicon and hydrogen is formed at -0.5 V, and a mechanism is proposed for the electrochemical evolution of hydrogen on silicon.

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Received 27th July 1960

DETERMINATION OF THE EQUILIBRIUM CURVES FOR BINARY MIXTURES OF ISOBUTANOL WITH *o*-, *m*-, AND *p*-XYLENES

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To determine the equilibrium curves for binary *o*-xylene-isobutanol, *p*-xylene-isobutanol, and *m*-xylene-isobutanol mixtures, the recirculation apparatus shown in Fig. 1 was used. It consisted of a cylindrical glass boiler *a* whose inner walls were lined with grains of ground glass 1–2 mm in diameter, fused on at the softening temperature. The apparatus was made from Rasotherm Jena glass. The upper part of the boiler was joined to a device *b* for the separation of vapour and liquid (separator) and the lower part via tube *c* to a device *d* for mixing the liquid and condensate.

The boiler was surrounded by asbestos cloth 2 mm thick, on the outside of which was wound a double nichrome heater spiral with a maximum permissible load of 300 W, thermally insulated with doubly wound asbestos cord 5 mm in diameter.

The cylindrical separator *b* had a central thermometer pocket surrounded by two concentric screens. The pocket and the inner screen had a corrugated surface designed to retain and return liquid droplets carried up by the rising vapour. The outer screen together with the separator wall served as the insulation.

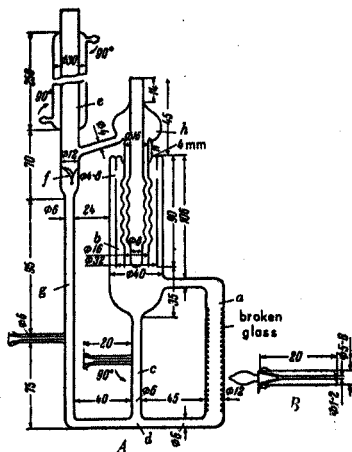


Fig. 1. A) Apparatus for the determination of liquid-vapour equilibrium; B) sidearm for sampling (ϕ = diameter in mm).

To achieve optimum thermal conditions for the operation of the apparatus, the outer wall of the separator was uniformly wound along its length, except for the collector at the top, with nickel wire 0.1 mm in diameter, serving as a resistance thermometer, followed by an insulating layer of asbestos cloth (5 mm thick) and asbestos cord (15 mm thick) and then a 200 W bifilar nichrome winding uniformly wound over the thermal insulation and the nickel resistance spiral. The upper part of the separator carried a collector *h* for the condensate, which was connected to a vertical water-cooled condenser *e*. At the lower part of the condenser there was a dropper *f*, with a large cross-section, joined via tube *g* with the mixer *d*, which was both simple and effective.

Tubes *c* and *g* had side-arms for the sampling of liquid or vapour, consisting of capillaries with an internal diameter of 1 mm and maximum length of 2 cm, closed with ground stoppers whose design made sampling both easy and rapid with minimum losses (Fig. 1B). The socket and stopper of one of the side-arms were marked with coloured glass to facilitate correct refitting after washing the apparatus.

The three coils were joined to three terminals mounted on the connecting tube. To facilitate removal from the electrical part of the apparatus, five connectors were fitted on the lower part of the condenser.

The electrical circuit (Fig. 2) consisted of two rheostats R_1 and R_2 controlling the supply of current to the two heaters, and a Siemens bridge supplied with alternating current known to within 3%, which served for the determination of the resistance of the nickel coil on the separator wall and hence, in conjunction with a calibration curve, of the temperature.

Principle of Operation

The apparatus is filled with the binary mixture through the top part of the condenser. On heating the boiler, the rising stream of vapour, in equilibrium with the liquid, passes into the separator, and liquid in the form of droplets, settling on the screen of the separator, returns via tube *c* to the boiler mixing on the way with the condensate, and then again vaporises.

Since the separator is heated, the vapour entering the collector does not condense, but it begins to lose heat, condensing eventually in the reflux condenser. The stream of condensate passes through the dropper to the mixer *d*. After some time a steady state is established in the system.

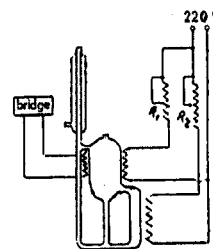


Fig. 2. Circuit of the electrical part of the apparatus.