

where Δ before a logarithm indicates the difference between analogous terms for the two acids being compared:

$$\begin{aligned}\Delta \ln K_H^* &= \ln K_H^* \text{ acid } x - \ln K_H^* \text{ standard acid;} \\ \Delta \ln (1 + K_H^* + K_{\text{con}}) &= \ln (1 + K_H^* + K_{\text{con}}) \text{ acid } x - \\ &\quad - \ln (1 + K_H^* + K_{\text{con}}) \text{ standard acid.}\end{aligned}$$

The formula shows that a differentiating effect will only be observed when there is a change in the ratio of the instability constants and conversion constants of the acids being compared.

On transfer of acids of different types from an aprotic solvent to water, the molecules of acid, which do not react with the solvent, form products with water, whose composition, polarity, and, hence, stability vary with the type of the acid in solution. Within the group of aprotic solvents such products are not formed and this factor has no influence.

The value of K_{con} also depends on the properties of the dissolved acid and the solvent. In aqueous solutions, where the solvent has a fairly pronounced proton affinity and the dielectric constant is high, K_{con} will tend to zero, but in aprotic solvents it will have an appreciable value and will vary with the dielectric constant of the solvent. However, the experimental data show that, within the group of aprotic solvents, this effect on different acids is the same and no differentiating action is observed.

SUMMARY

1. The relative dissociation constants of acids of two types (carboxylic acids and nitrophenols) in aprotic solvents (benzene, carbon tetrachloride, chlorobenzene, dichloroethane) are approximately the same, *i.e.* within the group of aprotic solvents no differentiating action is observed.
2. The differentiating action of aprotic solvents towards acids of different types compared to the behaviour of these acids in water has been explained in terms of Izmailov's theory.
3. The relative dissociation constants of acids, determined electrometrically and with indicators, do not agree; this is explained by ionic association in media of low dielectric constant.

OXIDATION OF THE GERMANIUM SURFACE IN CHEMICAL ETCHING

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The electrical and physical properties of the germanium surface are largely determined by the previous chemical treatment of the semiconductor. Numerous etches have been described in the literature, some of which are currently used in the industrial manufacture of semiconductor devices. These etches all contain a strong oxidising agent — either hydrogen peroxide or nitric acid. Thus the germanium surface after etching is always oxidised. After treatment in different etching agents, the surface properties of germanium (surface conductivity, surface recombination) vary. This shows that the character of the surface oxide depends on the type of etch^{1,2}.

Various studies of the properties of the germanium surface by chemical, optical, and electron-diffraction methods failed to reveal the composition and structure of the surface oxide layers.

In the present work a charging-curve method was used to study the oxidation of the germanium surface during etching.

EXPERIMENTAL

For convenience and reproducibility, all the experiments were carried out on degenerate polycrystalline germanium, containing not more than 0.01% of impurities. The apparatus for the determination of charging curves was described earlier³. The germanium electrode was etched for a given time, in a given etch, then it was washed with twice distilled water quickly, and transferred to a cell for measurement of cathodic charging curves. All the curves were taken in 0.1 N sulphuric acid at 20° with a cathodic current density of 10⁻³ A cm⁻².

The germanium surface oxidation during etching was studied in the following solutions: (1) etch CP-4: 50 cm³ HNO₃, 30 cm³ CH₃COOH, 30 cm³ HF, 0.6 cm³ Br₂; (2) Ellis's etch No.5: 40 cm³ HF, 6 cm³ H₂O₂, 24 cm³ H₂O; (3) Ellis's etch No.8: 20 cm³ HNO₃, 10 cm³ HF; (4) hydrogen peroxide etch: 20 cm³ H₂O₂, 1 mg KOH; (5) potassium dichromate etch: 20 cm³ HF, 10 cm³ HNO₃, 5 cm³ H₂SO₄, 50 cm³ H₂O, 1.5 g K₂Cr₂O₇, 1 g NaCl.

These etches were chosen for the following reasons. The CP-4, peroxide, and dichromate etches find extensive technological application. Ellis's etches (No.5 and No.8) have been comparatively thoroughly studied², optically and by electron diffraction. Thus, it is of interest to compare the results of Ellis with those obtained here from charging curves.

In Figs.1 and 2 are presented charging curves obtained with germanium etched for 15 and 60 sec in the etches shown. The Table shows the steady-state potentials of a germanium electrode in 0.1 N H₂SO₄ measured after 15 sec in a number of etches. The amounts of charge required to reduce the surface oxygen are also reported. The latter were obtained from charging curves for samples etched for 5, 10, 15, 30, and 60 sec. As can be seen from

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TABLE.

Etch	Steady-state potential (on the hydrogen scale), V	Amount of charge ($C\text{ cm}^{-2}$) required for reduction after etching for various periods				
		5 sec	10 sec	15 sec	30 sec	60 sec
CP-4	0.140	$3.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$9.0 \cdot 10^{-3}$
Ellis's No. 5	0.040	$2.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$
Ellis's No. 8	0.180	$5.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$
Peroxide	0.020	$5.0 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
Potassium dichromate	0.105	$1.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$

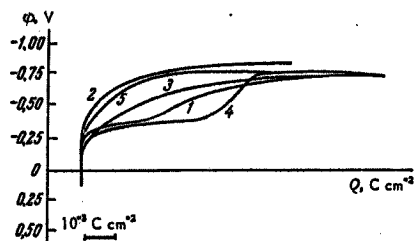


Fig. 1. Charging curves after 15 sec etching of germanium: 1) CP-4 etch; 2) Ellis's etch No. 5; 3) Ellis's etch No. 8; 4) peroxide etch; 5) potassium dichromate etch.

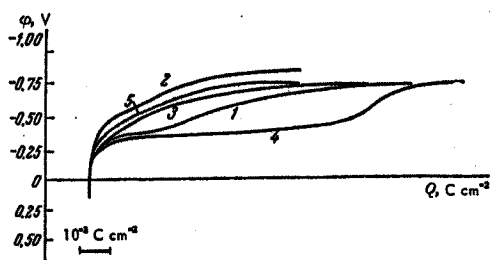


Fig. 2. Charging curves after 60 sec etching of germanium: 1) CP-4 etch; 2) Ellis's etch No. 5; 3) Ellis's etch No. 8; 4) peroxide etch; 5) potassium dichromate etch.

Figs. 1 and 2 and the Table, the course of the charging curves, the value of the steady-state potential, and the amount of charge required to reduce the surface oxygen, are a function of etching time and etch composition. This suggests that the character of the surface compounds is specific for each etch. For all the etches studied, except Ellis's etch No. 5, the arrest in the rise of the cathodic overpotential started at ~ 0.2 V. For etch No. 5, the start of the arrest was not sharp, and the hydrogen evolution potential for a germanium surface treated with this etch was about 0.10–0.25 V less negative than for a pure germanium surface (~ -0.75 V at $I = 10^{-3}$ A cm^{-2}).

Curves 1 and 4 in Figs. 1 and 2 correspond to the CP-4 and peroxide etches and differ from the curves for the other etches. In these curves at a potential of ~ -0.3 V a horizontal arrest appears and its length increases with etching time. This phenomenon is absent in the curves for all the other etches. The amount of charge required for the removal of surface oxygen depends on the etching time and was found to be between $\sim 1.5 \times 10^{-3}$ and 1.2×10^{-2} C cm^{-2} for all the etches studied. This is equivalent to 4–30 monolayers of oxygen³. Thus, one can suggest that surface oxides formed during etching constitute a separate phase. All these oxides are specific to each etch. The horizontal portion is largest for the peroxide etch (curve 4) and shows some structural homogeneity of the oxide, the germanium being obviously in the quadrivalent state. According to Ellis², treatment of germanium with etch No. 8 covers the surface with quadrivalent germanium compounds, which can be dissolved away with HF.

The absence of the horizontal portion in curve 3 in Figs. 1 and 2 shows that the structure of the oxide layer is inhomogeneous after etching in etch No. 8. It is of interest to note that treatment of the germanium sample in this etch for longer than 15 sec does not lead to an increase of charge required for reduction, which stays at $\sim 8 \times 10^{-3}$ C cm^{-2} , i.e. corresponds to 10 layers (calculated on the basis of GeO_2). The charging curve (curve 5) for the dichromate etch is similar to that for etch No. 8, though the amount of charge required for reduction is somewhat smaller. It appears that the structure of the films obtained with these two etches is very similar.

The CP-4 etch, which is used extensively in semiconductor technology, occupies an intermediate position. The oxide layer formed on germanium on treatment with CP-4 contains a significant amount of compounds with homogeneous structure, as seen from the flattened portion of the curve. According to Ellis², treatment of germanium with etch No. 5 leads to a homogeneous monoxide layer, which grows within 30 min to a thickness of 50 Å. The existence of such a layer is confirmed by curve 2 in Figs. 1 and 2. The film is not fully reduced on cathodic polarisation with a current density of 10^{-3} A cm^{-2} . The hydrogen overpotential is about 0.1 V higher than for pure germanium.

The steady-state potentials in 0.1 N H_2SO_4 for a germanium electrode, treated with different etches, are different. The smallest potential is given by the germanium electrode treated with the peroxide etch (0.020 V); the maximum value of potential is obtained by treatment with etch No. 8.

For germanium, etched with CP-4, No. 8, or dichromate etch, the steady-state potential moves to more positive values with increase of the oxide layer thickness. This phenomenon does not occur with germanium etched in No. 5 or peroxide, whose oxide films differ both in structure and composition from the films obtained from HF– HNO_3 mixtures.

It is known that oxide film formation on germanium takes place not only during etching but also on contact with air. Fig. 3 shows charging curves for a sample of germanium maintained in air for periods of 1, 2, and 4 h. This germanium sample was previously etched in CP-4 and subjected to a cathodic polarisation at a current density of 10^{-3} A cm^{-2} . The curves in Fig. 3 also tend to become horizontal at a potential of ~ -0.2 V. The amount of charge

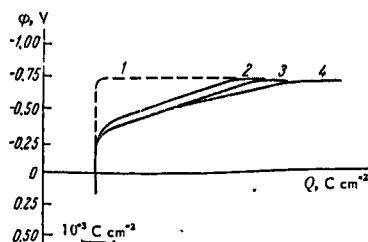


Fig. 3. Charging curves for cathodically polarised germanium after exposure to air: 1) no exposure to air; 2) exposed for 1 h; 3) exposed for 2 h; 4) exposed for 4 h.

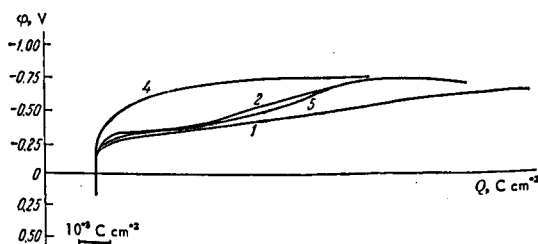


Fig. 4. Charging curves for a germanium sample etched in various etching agents for 15 sec and then exposed to air for 1 h:

- 1) in CP-4; 2) Ellis's etch No. 5; 3) Ellis's etch No. 8;
- 4) peroxide etch; 5) potassium dichromate etch.

required for reduction increases with the time of exposure to air, and corresponds to 4.3×10^{-3} , 5.0×10^{-3} , and 5.8×10^{-3} C cm $^{-2}$. If one assumes that the film formed in air, which is reduced at a potential of -0.2 V, corresponds to GeO $_2$, then the present results are in good agreement with those of Archer⁴, obtained optically. The thickness of the film on the basis of the data in Fig. 3 is 19, 22, and 25 Å, whereas Archer found, for the same time intervals, 19, 21, and 22 Å.

It is interesting that etching in CP-4 followed by cathodic treatment at a current density of 10^{-3} A cm $^{-2}$ ensures that the germanium surface is clean and free from surface oxide compounds. Curve 1 in Fig. 3, which corresponds to this case, does not show an arrest.

Fig. 4 shows cathodic charging curves for a germanium electrode, etched in various etching agents for 15 sec and then exposed to air for an hour. As can be seen from Fig. 4, in this case the action of all the etches, except the peroxide etch, leads to formation of an oxide film of almost identical composition. Thus the specific effects of the etches disappear on exposing the surface to air after etching.

In the case of germanium etched in peroxide the charging curve after exposure to air has a slightly different form (curve 4, Fig. 4). Apparently the structurally homogeneous oxides formed in peroxide etching undergo considerable changes on exposure to air and lose their homogeneity.

SUMMARY

1. Germanium surfaces etched in various etching agents were studied by means of charging curves.
2. Each etch leads to oxide films which are specific both as to structure and composition.
3. Etching in hydrogen peroxide leads to the most homogeneous film. The charging curves obtained after treatment with this etch show a clear plateau at a potential of ~ -0.3 V.
4. The specific effects due to all the etches, except for the peroxide etch, disappear on exposing the etched sample to air.

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FREE ENERGY CHANGE IN THE POLYMERIZATION OF LACTAMS UNDER STANDARD CONDITIONS† [LOW TEMPERATURE HEAT CAPACITIES OF LACTAMS AND OF POTASSIUM CHLORIDE]‡

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Although polymerisation of heterocyclic compounds is a relatively new branch of chemistry, thorough investigation of reactions of this type constitutes an urgent problem. In this connection the kinetics and heats of polymerisation of lactams and other heterocyclic compounds have been studied during recent years at the Thermochemical Laboratory of the Chemistry Faculty of Moscow State University.

The ability of heterocyclic compounds of the same series to polymerise varies sharply in relation to the number of atoms in the ring. For example, whereas the eight-membered ϵ -enantholactam is almost completely polymerised at 220° in the presence of a small quantity of activators,

† Fung Shih-yen and E. A. Seregin assisted in the experimental work.

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