ELECTROCHEMICAL INSERTION OF ALKALI METALS FROM THEIR MOLTEN CHLORIDES INTO SINGLE CRYSTALS OF SILICON

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The reactions proceeding on a single-crystalline silicon cathode in a molten eutectic mixture of lithium, sodium, and potassium chlorides were studied. On the basis of the results of polarization measurements and measurements of the relaxation of the current and the potential, coulometric, x-ray spectral, and chemical analyses, compared with micrographs of the surface of the single crystal, the basic characteristics of the electrochemical insertion of alkali metals into a semiconductor electrode were established.

The insertion of alkali metals into electrodes in the process of cathodic polarization was directed experimentally [1] and studied comprehensively for a number of metallic electrodes (Pb, Ni, V, Al, and others), both in aqueous and nonaqueous solutions and in molten salts [2]. It was established that the process of insertion leads to the formation of a surface alloy of the inserted element with the cathode material; the kinetics of the process is determined to a substantial degree by solid-phase diffusion of the components in the electrode; at sufficiently negative potentials, the insertion process is responsible for the cathode atomization of the electrode material [1].

The purpose of this work was to investigate the cathodic insertion of alkali metals into single-crystalline semiconductor electrodes. We assumed that the elucidation of the typical and specific peculiarities of the process of cathodic insertion in this case would be extremely useful for construction of the general picture of this important class of electrode reactions. Moreover, the electrochemical insertion of impurities into a semiconductor may find use as a method of measured introduction of additives and investigation of the behavior of impurities, as well as the method of studying the interaction in the system impurity–semiconductor and diffusion processes in the volume of the semiconductor.

The use of molten inorganic salts provides great possibilities for conducting the process of cathodic insertion of metals into a semiconductor; in this sense the most valuable qualities of salt melts are: high electric conductivity, absence of proton carriers, permitting the electroreduction of a large number of cations up to the most electronegative (Li, Na, K, Mg, Al) and high temperatures, which accelerate the processes in a solid.

EXPERIMENTAL METHODS AND RESULTS

Below are outlined the results of an investigation of the cathodic insertion of alkali metals into single crystalline silicon from a molten eutectic mixture LiCl–NaCl–KCl. All the experiments were conducted in a hermetic cell in an atmosphere of argon above a melt at 380-400°C. Plates of a single crystal of Si [111] with a clamped contact on the current lead, immersed in the melt, served as the working electrode. The plates were treated according to standard technology [3]. The auxiliary electrode was a cylinder of glass carbon, the reference electrode a half-cell Ag/5 mole % AgCl in LiCl–KCl–NaCl ($\varphi_{Ag/Ag+} = -1.12$ V relative to a standard chloride electrode[4]). The electrolyte was prepared in the working cell by melting on anhydrous salts in a stream of argon in a ratio 38 (KCl), 8.5 (NaCl), 53.5 (LiCl) mole %.

The electrochemical measurements included recording of the static polarization curves and the switching on curves i vs t or φ vs t with a P 5611 potentiostat, as well as coulometric analysis. The content of the

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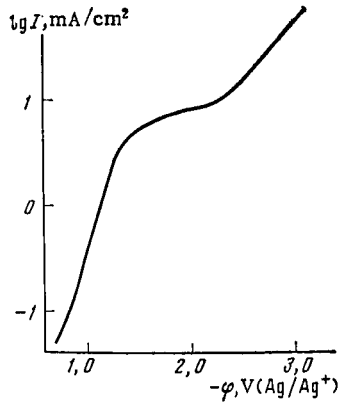

Fig. 1. Cathodic volt–ampere curve of a single crystalline Si electrode (n is the type; 4.5 Ω · cm, face [111]) in a molten mixture of KCl–NaCl–LiCl at 400°C.

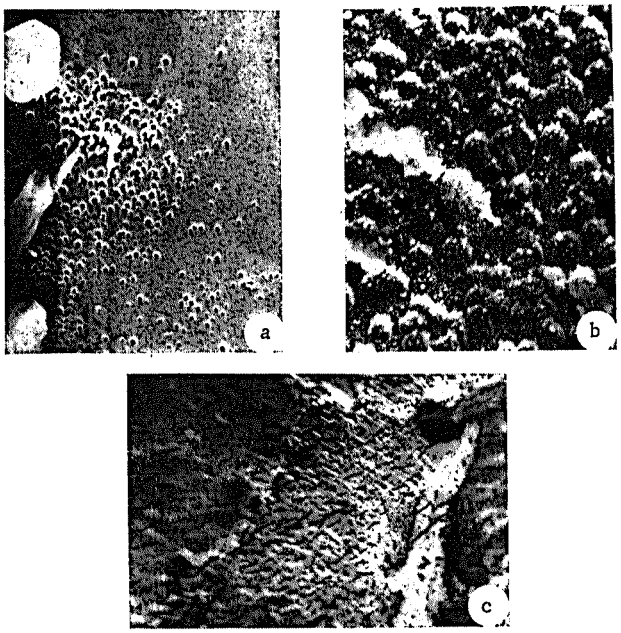

Fig. 2. Micrographs of the state of the surface of silicon after prolonged exposure (1 h) at the potentials corresponding to the first (a), second (b), and third (c) portions of the polarization curve.

alkali metals in Si was monitored by an optical method (flame photometry of Si samples dissolved in a mixture of HF and HNO_3), by an x-ray spectral method on a microanalyzer from Samesa and an ISM-50A from JEOL. The morphology of the electrode surface and the distribution of inserted potassium through the depths of the electrode were also investigated on the last instrument.

When single crystalline Si is inserted in the investigated melt, a static potential is established on it (φ_{st}), the value of which varies from −0.4 to −0.62 V, depending on the state of the surface of the single crystal, the presence of a damaged layer, defects on the ends of the working electrode, as well as the accumulation of products of electrolysis in the melt. In cathodic polarization of Si in a static potentiostatic system, we obtained i vs φ curves; one of them is cited as an example in Fig. 1. Usually such curves contain three typical portions: a region of potentials from φ_{st} to $\varphi \simeq -1.2$ to −1.3 V, where a Tafel straight line is observed in a plot of log I vs φ with a slope b = 0.23-0.33 V (α = 0.4-0.6) for different samples. When the potential is further shifted into the cathodic region, there is an increase in the current; it reaches a limiting value at φ = −1.5 to −2.4 V (second portion). The value of the limiting current is well reproduced for various samples and is 5-7 mA/cm²; on this portion the appearance of small oscillations and flareups of the currents is characteristic. Mixing of the melts

TABLE 1. Results of Analysis of a Silicon Electrode after Polarization

−φ, V	D, mA/cm²	c_{Li}, at.% data of photometry	c_{K^+}, at.%, data of x-ray spectral analysis	Δp, g/h
0,62	0	0,05	0,002	–
0,70	0,006		0,009	0,00017
0,80	0,2	0,1	0,006	0,00022
0,90	0,3		0,05	0,00024
1,20	0,5	0,07	0,04	0,00031
1,80	1,6	0,07	0,05	0,00060
2,80	2,1	0,11	0,056	0,0000
3,00	2,3			−0,0001
4,5	4,0		0,036	−0,00036

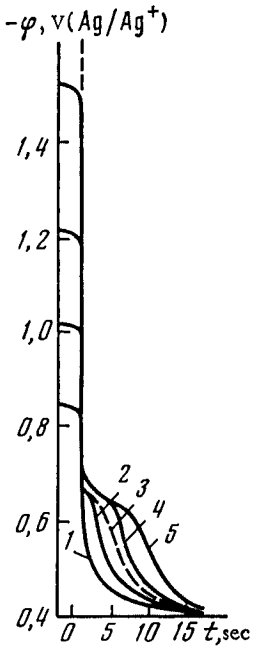

Fig. 3. Switching on curves of φ vs t for a single crystalline Si electrode in molten KCl−NaCl−LiCl (400°C) after preliminary cathodic polarization (t ~ 300 sec) at the potentials 0.84 (1), 1.0 (2), 1.2 (3), 1.5 (4), 1.6-1.8 V (5) (according to a Ag/Ag^+ reference electrode).

with a stream of argon leads to a certain increase in the value of I_{lim}, probably associated with a change in the geometrical size of the surface of the sample bathed by the melt. On the third portion of the polarization curve (φ more negative than −2.0 V), a new linear increase in the current is observed, accompanied by substantial fluctuations of the current.

Simultaneously with the recording of the polarization characteristics, we made an analysis of the state of the surface of the working electrode. It was found that on the first portion the change in the surface morphology is negligible, on the second portion there is a substantial loosening of the Si surface, while on the third a highly developed roughness arises, and in certain sites of the surface, etching pits characteristic of the given crystallographic orientation can be detected (Fig. 2). It should also be noted that the result of such cathodic treatment at φ more negative than −2.6 to −2.8 V is the visually observed atomization of the Si surface and the accumulation of a finely divided dark gray powder in the electrolyte. Moreover, we monitored the change in weight of the Si sample after prolonged (2-3 h) cathodic polarization at the potential of each of

the portions noted. The results of the measurements are cited in Table 1 and are evidence that the insertion of alkali metals already begins on the first portion (at $\varphi < -0.7$ V)' and becomes quite noticeable in the region of the second portion, all the way down to $\varphi = -2.8$ V. It is characteristic that at more negative potentials, in the region of cathodic atomization, a decrease in weight of the Si plates is observed.

In supplementation to these data, Table 1 cites the results of a determination of the content of alkali metals in Si, obtained by the method of flame photometry (the Si electrodes were washed free of the melt remaining on the surface layer, then dissolved entirely in a mixture of HF and HNO_3, the solution evaporated to dryness, and the residue dissolved in dilute HNO_3), as well as the data obtained by the x-ray spectral method for the average K^+ content over the surface in the investigated samples. It should be noted that to verify the quality of washing of the melts from the samples, after cathodic polarization, the Cl^- content on the surface was monitored by x-ray spectral analysis. The results showed a practically complete absence of Cl^- on all the investigated samples. From Table 1 it also follows that the concentration of Li^+ and K^+ in the volume of the samples after cathodic polarization significantly exceeds their concentration in the initial samples. Measurements performed on an ISM-50A instrument also permitted a determination of the depth of penetration of K^+ into the investigated samples, which is 5-10 μ. The data of x-ray spectral analysis confirmed the presence of K^+ in the surface layer and showed the nonuniformity of its distribution on the surface of the sample, and, moreover, revealed the accumulation of traces of other metals (Ca^{2+}). Thus, the results obtained pertain to alkali metals inserted into the volume of the crystals.

The nature of the process of cathodic insertion can also be judged according to the dependence of the potential drop with time for preliminarily cathodically polarized samples of Si. A typical view of such φ vs t curves for various portions of the i vs φ curves is cited in Fig. 3. On the curves there is a lag in the potential at $-\varphi = 0.6$-0.7 V. The potential -0.7 V can be considered as the equilibrium potential of combination of an alkali metal (Li, K) with Si. The duration of the lag increases somewhat with transition to the second portion, remains practically constant in the region of the limiting current, and then decreases with transition to the region of cathodic atomization.

DISCUSSION OF RESULTS

The aggregate of data cited is evidence that during cathodic polarization of silicon in the investigated melts, parallel processes of insertion of metals into the single crystal and cathodic atomization of the surface occur in the presence of an admixture of oxidizing agent – O_2, H_2O – which can be arbitrarily expressed by the following reactions:

$$Me^+ + e + Si_s \rightarrow MeSi_s, \quad (1)$$

$$n\,Me^+ + e + Si \rightarrow Me_nSi, \quad (1a)$$

i.e., cathodic insertion with the formation of a film of a compound or solid solution and diffusion of the inserted alkali metal deep into the electrode. The reaction with an oxidizing agent

$$Me_2Si + 3O = Me_2SiO_3 \quad \text{(dispersed)} \quad (2)$$

$$Me_nSi + n/2H_2O = n/2Me_2O + Si \quad \text{(dispersed)} \quad + n/2H_2 \quad (3)$$

and with a melt

$$n\,Me^+ + Me_nSi_m = n\,Me_2^+ + Si_m \quad \text{(dispersed)}. \quad (4)$$

The scheme cited above at potentials more negative than the equilibrium potential for the given alkali metal can be supplemented by reactions of electrochemical deposition of alkali metals in pure form and their chemical reaction with the components of the melt with the formation of subions Me_2^+ [5].

The kinetic model of the process at low cathodic potentials, corresponding to the enumerated equations should be limited by the formation of a surface alloy. As is shown by Fig. 1, a Tafel straight line with slope 0.23-0.33 V ($\alpha = 0.4$-0.6) corresponds to this portion, while the exchange current related to the equilibrium potential of the alloy formed ($\varphi = -0.7$ V), is equal to $\sim 10^{-3}$ A/cm^2. Let us note that the equilibrium potential of the compound of silicon with lithium or potassium formed during insertion (-1.8 V relative to the normal chloride electrode) is less negative than, for example, the known equilibrium potential of the intermetallic compound $NaPb_3$ (-2.6 V relative to the normal chloride electrode) – one of the most noble alloys of the alkali metals [1].

To determine the nature of the limiting current on the second portion, it is important to analyze the dependence of the amount of the electroactive compound accumulated on the surface on the potential and time of electrolysis, as well as the data cited in Fig. 2, indicating a loosening of the silicon surface during prolonged electrolysis. Judging by the time lag on the φ vs t curves of anodic dissolution of the surface alloy, a weakly potential dependence charge $Q \sim (1\text{-}5) \cdot 10^{-3}$ C/cm^2 corresponds to the accumulation of a film of alloy on the surface on the second portion, and, consequently, the total amount of the electroactive surface compound depends little on the potential. This means that the observed limiting current corresponds to the step of a chemical reaction of the surface alloy with the oxidizing agent impurity (or with the melt); the presence of chemical dissolution of the film stabilizes its static thickness at the level $\delta \leq 10^2$ Å, and in prolonged electrolysis leads to a loosening of the surface; under these conditions the step of diffusion of the alkali metals is not limiting for the corresponding reactions (3) and (4), and the kinetic limiting current is in the range $(5\text{-}7) \cdot 10^{-3}$ A/cm^2.

In addition to the formation of a surface film, the data that we obtained are evidence of the penetration of alkali metals into a single crystal of silicon; in this case the concentration of the solid solution formed with respect to Li^+ and K^+ is evidently comparable with the limiting solubility of these metals in Si [6]. The results of measurements of the mobility of Li^+ and K^+ ions in an Si single crystal, systematized in [6, 7], give the following values for the diffusion coefficients at 400°C: $D_{Li(Si)} \simeq 2 \cdot 10^{-8}$ cm^2/sec and $D_{K(Si)} \simeq 2.5 \cdot 10^{-9}$ cm^2/sec, so that during electrolysis ($t \sim 2 \cdot 10^2$ sec), the diffusion front extends to a depth $\delta \sim \sqrt{Dt} = 20\ \mu$ (Li^+) or $7\ \mu$ (K^+). Let us note that direct measurements of the distribution profile of K^+ along the fracture surface of Si is in good agreement with the estimates cited.

We also found that the nonsteady-state process of formation of a solid solution of the metal in Si makes an appreciable contribution to the relaxation i vs t curves in the case of potentiostatic switching on of the cathodic current. Thus, the law of relaxation of the current in a plot of i^2 vs $1/t$ is linear, and the slope depends weakly on the potential and is $f \simeq di^2/d(1/t) = (5\text{-}8) \cdot 10^{-10}$ A · sec/cm^4. When this value is compared with the theoretical, it should be kept in mind that the classical concepts can be applied to diffusion in the solid phase only in the case of small amounts of the diffusing substance, far from the limit of solubility of the impurity in the crystal. If we consider that the mobility of Li^+ in Si is the greatest [6] and $D_{Li(Si)} \simeq 2 \cdot 10^{-8}$ cm^2/sec [7], we obtain a slope $f \sim 3 \cdot 10^{-9}$ A^2 · sec/cm^4, and thus, the theoretical estimate even somewhat exceeds the experimental values. Thus, the diffusion currents observed on the cathodic i vs φ curves of a single-crystalline silicon electrode in molten LiCl–NaCl–KCl are due to removal of atoms of the inserted alkali metal from the surface into the depths of the Si single crystal.

The behavior of Si at high cathodic potentials is determined by the intensity of the liberation of liquid alkali metals, which are good mordants for semiconductor single crystals [8] and intensively break down the Si surface, revealing primarily structural defects in the surface layer of the sample.

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