MECHANISM OF CHARGE TRANSFER DURING ANODIC OXIDATION OF THIOSULPHATE IONS ON GERMANIUM SEMICONDUCTOR-ELECTROLYTE INTERFACE

C. S. Singh, M. V. Ramanamurti and M. M. Singh

Banaras Hindu University Varanasi-221005

(Received 10 Dec. 1977; accepted March 1978)

The mechanism of electron transfer between germanium semiconductor and thiosulphate ions in the electrolyte during their oxidation on n⁻and p⁻Ge anodes has been elucidated from the polarization measurements. The test solutions consists of 0 02M to 0.50M sodium thiosulphate in 0.1M phosphate buffer solution (pH = 7 2) The Tafel relation, $\eta = a + b \log CD$, is valid in a narrow range of CD. The saturation current density is observed only on the polarization curve of n⁻Ge anode. which increases on addition of the reductant to the supporting electrolyte and also on illumination of the electrode surface. The polarization curves for p⁻Ge remain unaffected in either of the two conditions. The participation of conductance band electrons during oxidation of thiosulphate ions has been concluded from the above studies.

The mechanism of electron transfer at semiconductor-electrolyte interface during the oxidation and reduction of the ions in the electrolytic solutions depends upon their redox potential along with the usual dependence on the applied potential and equilibrium concentration of electrons and holes. The oxidation reactions, in particular, occur with the simultaneous dissolution of electrode material and the kinetics of the overall reaction is governed by the nature of the current carrier involved. These two processes may or may not be competitive depending upon the fact that they involve the same or different current carriers Some typical light sensitive saturation current density [1–4] is usually observed on one or other type of electrode which may be further modified under the influence of two different processes occurring together at the same surface of the electrode. The comparison of the behaviour of polarization curves for n⁻and p⁻Ge semiconductor electrode in different conditions satisfactorily leads to the mechanism of the reaction under study.

In the present communication the mechanism involved in the oxidation of thiosulphate ions at the surface of germanium electrodes has been dealt to ascertain the nature of current carrier involved.

EXPERIMENTAL

The results of anodic polarization measurements have been recorded galvanostatically in the stirred solution. The electrochemical cell assembly[5] consisting of a germanium electrode, a platinum auxilliary electrode and saturated calomel electrode with a luggin capillary was placed in a wooden air thermostat maintained at 25±0.01°C. The experiments were carried in dark and for light illumination a pyrex mercury vapour lamp operated at 240 Volt (D.C.) was used. The detailed experimental procedure were the same as described earlier[6].

The germanium single crystals were supplied by Mullard limited (London). The type of conductivity, resistance and crystallographic orientation were determined by usual procedures[5]. The chemicals used were B.D.H. Analar grade, recrystallized in conductivity water before use. The pH of phosphate buffer used as supporting electrolyte was found to be 7.2. The buffer solution was purified by pre-electrolysis. The thiosulphate solution were standardized iodometically as suggested by Vogel[7].

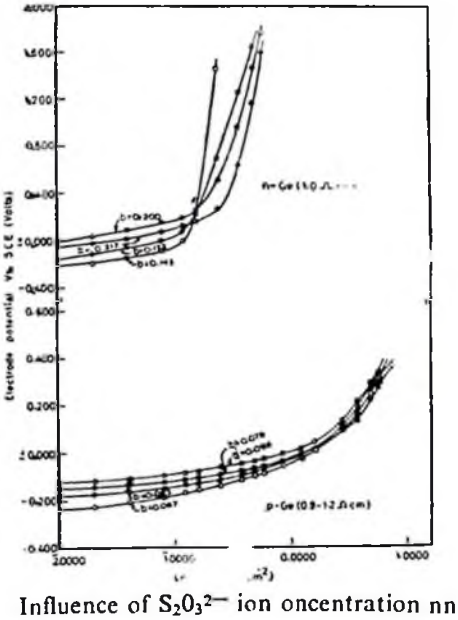


Fig. 1. Influence of $S_2O_3^{2-}$ ion oncentration nn anodic polarization of Ge⁻electrodes in 0 10M phosphate buffer of pH = 7.2 at 25°C.

—0.50M Sodium thiosulphate
—0.10M Sodium thiosulphate
● 0.02M Sodium thiosuiphate
○ —0.10M Phosphate buffer.

RESULTS AND DISCUSSION

The results of anodic polarization measurements for p⁻ and n⁻Ge anodes in 0.10M phosphate buffer containing different concentrations of sodium thiosulphate are illustrated in Fig. 1. The curves obey the Tafel relation up to about 0.120 mA cm^{-2} for n⁻Ge anode (the range of linearity decreases with the concentration of reductant) and about 0.840 mA cm^{-2} for p⁻Ge anode. On n⁻Ge anode the values of b increases with concentration of thiosulphate ions and all these values are greater than those obtained in the absence of the reductant. The value of b in the absence of the reductant is 0.145 V per unit of CD on n⁻Ge while on p⁻Ge anode it is 0.067 V per unit of CD.

The overpotential is increased with the addition of the reductant and this increase in overpotential depends upon the concentration of the reductant on both n⁻and p⁻Ge anode with an exception for 0.10M thiosulphate solution on n⁻Ge anode. A careful examination of the curves obtained for the polarization of n⁻Ge anode reveals that at first instant there is a gradual increase in the overpotential with increase in current density, but afterwards at higher CDs, the overpotential increase rapidly and enormously with small change in current density. This shows the occurrence of saturation current density at n⁻Ge anode. Further, the saturation current density linearly increases with the concentration of the reductant. The increase in the saturation current density is a function of the thiosulphate ion concentration. At p⁻Ge anode the overpotential increases steadily with current density and no saturation current density is obtained.

When biased anodically, the dissolution of both n⁻and p⁻Ge occurs in the phosphate buffer solution. For such a reaction, a saturation of current density is expected on the electrode with minority carriers participating in the reaction[8]. Our results show saturation of current density on n⁻Ge anode, which indicates that holes are consumed during the dissolution in phosphate buffer, similar to those obtained for dissolution in acid and alkaline media[9,10]. The holes in n⁻Ge, being the minority carrier, can move due to diffusion only and the potential falls completely in the space-charge region. When the rate of diffusion of holes equals the rate of dissolution, saturation of current density is reached. In p⁻Ge, on the other hand, holes are majority carriers and their drift is dependent upon the applied electric field, consequently the potential falls in Helmholtz region. Therefore, the polarization curves obey Ohm's law and potential increases steadily with current density.

On addition of thiosulphate ions to the phosphate buffer solutions, two reactions, viz., dissolution of anode material and oxidation of thiosulphate ions occur simultaneously. The curves obtained as such on two germanium anodes are likely to be influenced under two different reactions. A marked change has been observed on n⁻Ge anode with respect to the magnitude of saturation current density, whereas no change is predictable on p⁻Ge anode. The dissolution saturation current density increases during oxidation of thiosulphate ions. The increase in saturation current density shows that the two processes must occur through the participation of different current carriers. For instance, had the valence band electrons participated, the saturation current density should have been additive and consequently a decrease in current must be obtained[11], since, in this case both processes compete for holes and an inadequate supply of holes will cause a decrease in saturation current density.

Contrary to the above, the curves show an increase in the saturation current density which confirms that holes are not involved in the oxidation process. The results may be very well explained in the frame work of conductance band mechanism. If conduction band electrons participate, the electron will be transferred from the ion to the conductance band. As a consequence, an electric field will be developed at the surface of germanium electrode which causes the drift of holes from the bulk of germanium semiconductor to the interface[12]. And thus the holes appearing at the electrode surface due to drift will be simultaneously consumed by the dissolution process causing an increase in the saturation current density.

In p⁻Ge electrode the electrons are in minority and therefore, the addition of electrons to the conductance band during oxidation will not produce sufficiently strong electric field to cause the drift of holes in the valence band. Secondly, p⁻Ge anode being highly rich in the hole concentration, these extra hole produced at the interface will not change the nature of polarization curve. The curves obtained, both in the presence and the absence of the reductant are,

consequently, identical and confirm our expected mechanism. Moreover, these results are exactly similar to those obtained for the anodic oxidation of oxalate ions which involves conduction band electrons[13]. Hence, the oxidation of thiosulphate ions seems to proceed through the participation of conduction band electrons.

The addition of the reductant produces an appreciable change in the overpotential on n⁻Ge; but a small change on p⁻Ge anode. This shows that the two processes, the dissolution and oxidation of reductant occur at almost the same potential on p⁻Ge but at different potentials on n⁻Ge. The values of 'b' increase abruptly at n⁻Ge than at p⁻Ge, which shows that the rate of dissolution of n⁻Ge is considerably influenced during the oxidation of thiosulphate ions as compared to p⁻Ge.

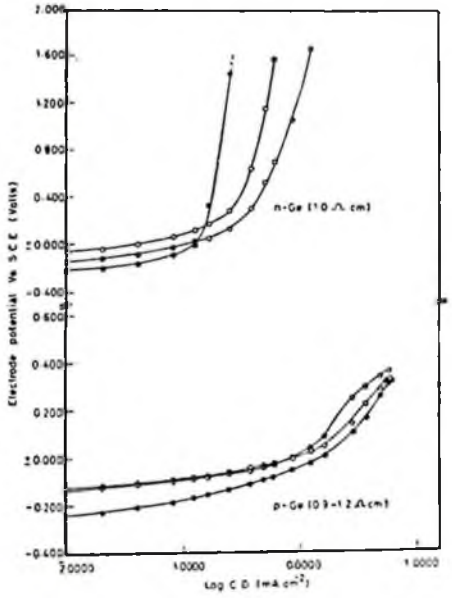


Fig. 2. Effect of illumination on the anodic polarization of Ge⁻electrodes in 0.50M Sodium thiosulphate dissolved in 0.10M phosphath buffer of pH = 7.2 at 25°C.

● — In dark for phosphate solution
○ — In dark for phosphate buffer containing sodium thiosulphate.
— Illminated.

Fig. 2 represent the effect of illumination on both types of germanium anodes in the presence of the reductant in 0.10M phosphate buffer solution. The saturation current density on illumination increases on n⁻Ge anode, while there is no appreciable change in the nature of curve on p⁻Ge anode.

Our assumptions are finally supported from the above observations of the polarization behaivour of n⁻ and p⁻Ge anodes. Whereas the nature of polarization curves of p⁻Ge remains unaltered, the saturation current density observed on n⁻Ge anode, is increased further on illumination. The illumination of electrode surface induces the same effect as that induced by the oxidation process. The electrons are transferred from valence band to conductance band increasing the number of holes in the valence band[14]. Also, the electron transferred to conduction band accelerate the movement of holes towards the interface. Both result in an increase of saturation current density. Our findings are in accordance with the theoretical treatments and confirms the conductance band electron participation.

Acknowledgement :-The paper is dedicated to Late Dr. D. Singh, D. Sc., Ex⁻Reader, Department of Chemistry, B.H.U. who gave the impetus for the present work. The authors are thankful to Prof. O.P. Malhotra, Head, Department of Chemistry and Prof. C.V. Agarwal, Incharge, Basic Science, Institute of Technology, B. H. U. for necessary facilities and encouragements.

REFERENCES

1. W. H. Brattain, and C. G. B. Carret, Bell. Syst. Tech. J., 34 (1955) 129.
2. D. R. Turner, J. Electrochem. Soc., 103 (1956) 252.
3. E. A. Effimove and I. G. Erusalimchik, Zhur. Fiz. Khim., 32 (1958) 1103.
4. M. Green, J. Chem. Phys., 31 (1959) 200.
5. D. Singh, and A. N. Dwivedi, Z. Physik. Chem. NF., 72 (1970) 259.
6. M. M. Singh, and D. Singh Acta Chim. (Budapest), 87 (1) (1975) 51.
7. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis" 3rd Ed. Longmans Green and Co., pp. 349 (1961).
8. E. A. Effimov, and I. G. Erusalimchik, Zhur. Fiz. Khim., 32 (1958) 413.
9. F Beck, and H. Gerischer, Z. Elektrochem., 63 (1959) 500.
10 R. M. Lazorenko-Menevich, Doklady Akad. Nauk. SSSR., 144, (1962) 1094.
11. H. Gerischer, and F., Beck, Z. Physik. Chem. NF., 13 (1957) 389.
12. E. A. Effimov, and I. G. Erusalimchik, Zhur. Fiz. Khim., 35 (1961) 543.
13. M. M. Singh, and C. S. Singh, Acta Chim. (Budapest) (In press).
14. H. U. Harten, Electrochemica Acta., 13 (6), (1968) 2555.

Asian Paints' Research and Development are more than surface deep

Equipped by one of the finest labs in the country, our technical research and development wing keeps in close touch with newest trends in surface coatings. Import substitution with indigenous materials has been a tradition with us.

Fundamental research on raw materials has resulted in putting to use unconventional materials available in India.

This costs the Company a few lakhs annually. But then we don't grudge the expense. Our research boys are doing so well there.

Projecting tomorrow's marketing needs, analysing the trends of consumer behaviour for this country's size, is a gigantic job. Professionals in the field keep the facts at fingertips. EDP facility makes the task easier.

Development of materials for mass markets is our commitment.



ANY SURFACE THAT NEEDS PAINTING
NEEDS asian paints

AIYARS-A. 178