ELLIPSOMETRIC STUDY OF THE INTERACTION
OF A GERMANIUM MONOCRYSTAL WITH BROMINE

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Using an ellipsometric technique, the dynamics of formation of
adsorption layers in the process of interaction of bromine with a
germanium monocrystal surface has been studied. It is shown that the
reaction begins only when the second layer of bromine molecules is
formed on the germanium surface. The ellipsometric data are in
agreement with the results obtained by kinetic experiments.

Эллипсометрическим методом исследована динамика ад-
сорбционных заполнений во время химической реакции
германия с бромом. Сделан вывод о том, что химичес-
кая реакция германия с бромом становится возможной
только при адсорбции второго слоя молекул брома. По-
лучено хорошее соответствие между результатами ки-
нетических и эллипсометрических экспериментов.

Ellipsometry is an efficient method for studying heterogeneous chemical
reactions /1, 2/ since ellipsometric measurements can be carried out in agressive
media over a wide range of temperatures and pressures and provide information
on the surface state and the dynamics of adsorption coverage. In the present paper
an ellipsometric study of the interaction between Ge and gaseous bromine is
reported.

The experiments were performed using a set comprising an automatic
ellipsometer /3/ and an ultra-high vacuum reaction chamber provided with a
system of oil-free evacuation. The pressure of residual gases in the chamber was

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equal to 1×10^{-8} - 5×10^{-9} Torr. Bromine used in the experiments was purified according to a known procedure /4/. The surface of Ge monocrystal samples with large verge orientation in the direction {111} was cleaned by vacuum evaporation of germanium sulfide films /5/. The samples were electrically heated and the temperature was determined according to resistivity using a four-probe method.

A quantitative analysis of the ellipsometric data was performed utilizing approximate Drude equations giving, as shown by Bootsma and Meyer /6/, satisfactory results in the sub-monolayer region. According to the Drude model,

$$\Delta \delta = \overline{\Delta} - \Delta = \xi d \tag{1}$$

$$\delta \Psi = \overline{\Psi} - \Psi = -\eta d \tag{2}$$

$$d = d_m \theta \tag{3}$$

where $\overline{\Delta}$ and $\overline{\Psi}$ are the polarization angles characterizing a clean surface; Δ and Ψ are the polarization angles characterizing the substrate-adsorbed layer system; d_m is the thickness of the monolayer of adsorbed molecules; θ is the surface coverage. The coefficients ξ and η were calculated according to Drude's formulae /2,6/.

The first series of experiments was performed at room temperature of the samples. It was shown that the adsorption of bromine molecules on the germanium surface resulted in a decrease of polarization angles Δ and Ψ, while the ellipsometric theory predicts an increase in Ψ and a decrease in Δ. This anomalous behavior of Ψ upon the adsorption of various gases on clean surfaces of Ge and Si was reported earlier in /6,7/. It was interpreted as a result of rebuilding of the surface layer of atoms in a semiconductor crystal under
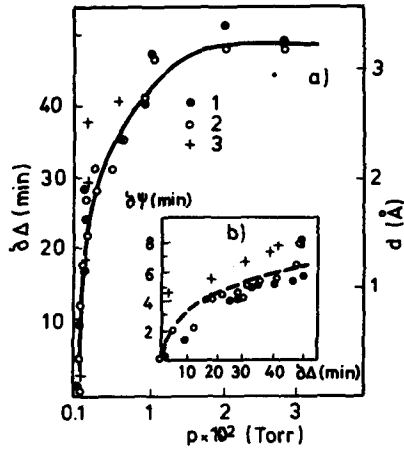
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Fig. 1. a) Ellipsometric angle $\delta\Delta$ and thickness of the adsorption layer vs. the pressure of bromine at T = 20°C for three samples; b) $\delta\Psi$ vs. $\delta\Delta$ at T = 20°C

chemisorption /8/. Owing to anomalous changes in Ψ , for a quantitative analysis of the effective thicknesses of adsorbed layers d, only data on the change of the polarization angle Δ have been used. The appreciable scatter of the experimental Ψ data (Fig. 1b) can be explained by the fact that polarization angle Ψ is more sensitive to changes in the substrate properties, while angle Δ is more sensitive to changes in the thickness of the adsorbed layer /2/.

Figure 1a shows the dependence of $\delta\Delta$ and the thickness of the adsorbed layer on the pressure of bromine vapours, the maximum change in polarization angle Δ being taken for every value of pressure (the dependence of $\delta\Delta$ on time at constant pressure has the form of saturation curves). Removal of bromine vapours down to 10^{-8} Torr did not result in a reverse change of Δ at any observed value of $\delta\Delta$. This indicates the irreversibility of the adsorption process. The maximum thickness of the adsorbed layer at room temperature was about $\simeq 3.5$ Å. To explain this value, two arrangements of the bromine molecule on the Ge-surface
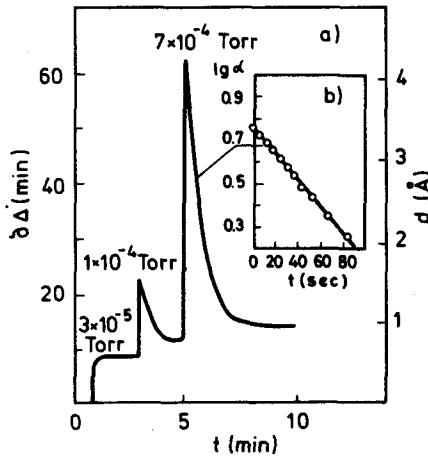
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Fig. 2. Ellipsometric angle $\delta\Delta$ and thickness of the adsorption layer vs. time at different pressures of bromine (T = 190°C)

should be considered. The molecule of Br_2 representing a "dumbbell" in form can be parallel or normal to the surface, the monolayer thickness being determined by the dimensions of the "dumbbell". For the parallel orientation of the Br_2 molecule $d_m \simeq 2.2$ Å, and for its normal orientation $d_m \simeq 4$ Å /9/. Thus, the ellipsometric data obtained at room temperature can be interpreted as a result of adsorption of one monolayer with normal orientation of the Br_2 molecules or of two monolayers with parallel orientation.

Experimental dependences of $\delta\Delta$ and d upon time typical in the temperature range from 150 to 300°C are plotted in Fig. 2 at different pressures of Br_2 vapour. Bromine was fed into the chamber in small portions with subsequent evacuation upon achieving the required pressure; this resulted in an irreversible change of the polarization angle Δ , but when the portions of Br_2 were relatively large, the change of Δ was reversible. When filling the chamber, a rapid change of the angle Δ took place, while the rate of the reverse change of Δ was significantly
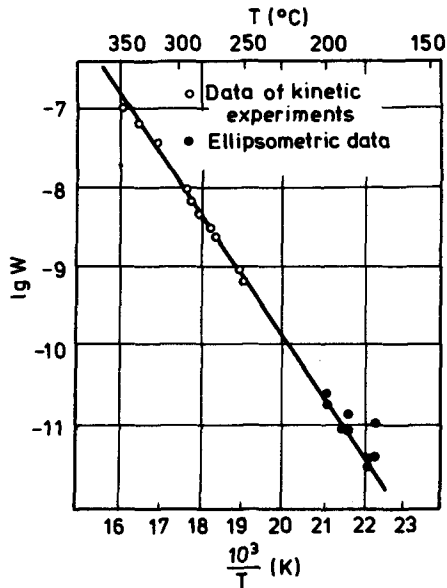
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Fig. 3. Dependence of the rate of germanium – bromine reaction on temperature in Arrhenius coordinates. o – kinetic data; ● – ellipsometric data

lower than that of Br_2 evacuation. This indicates that the curve for the reverse change of Δ describes the slowest stage of the process. This stage may be either a chemical act in the adsorption layer or desorption of the reaction products.

The presence of a region with irreversible changes in Δ might indicate that adsorption of one layer of Br_2 molecules is insufficient for the Ge–Br_2 reaction to occur. This agrees with earlier results /10/, where on the basis of kinetic data a possible mechanism of this reaction was proposed. However, as is seen from Fig. 2a, the values $\delta\Delta$ and d in the region of their irreversible change are smaller than expected for the full monolayer. This indicates that not all of the surface Ge atoms take part in the chemical reaction. In our experiments the number of chemically active surface atoms was equal to 1×10^{14} - 5×10^{14} cm^{-2}. The slowest stage is described by a first order kinetic equation (Fig. 2b). The rates of

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the Ge-Br$_2$ reaction obtained in kinetic experiments /10/ and those calculated from ellipsometric data can be described by a single Arrhenius dependence (Fig. 3), which also confirms the agreement between the kinetic and ellipsometric data.

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