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Abstract

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OBSERVATION OF AN E.M.F. DURING EPITAXIAL GROWTH OF GERMANIUM ON GERMANIUM USING A GAS-TRANSPORT REACTION WITH WATER

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In the epitaxial growth of semiconductor films from the gas phase, the supply of the crystallizing substance to the substrate is carried out by means of pyrolytic decomposition reactions, displacement reactions, reduction reactions, and most often by means of reversible gas-transport reactions (1). In the latter case, the transfer of substance from the source to the substrate usually proceeds according to the following scheme: the carrier reagent reacts with the substance of the source, located in the hot temperature zone, and the volatile reaction product diffuses or is transported in the stream of the carrier gas into a colder zone, where the substrate is located. As a result of the shift of chemical equilibrium, crystals of the transported substance form on the substrate and the carrier reagent is regenerated; it diffuses back to the source, and the cycle is repeated again. The literature gives overall schematic equations for certain gas-transport reactions, but, as a rule, the authors note that the actual mechanism of these reactions is unknown (2,3).

The role of electrochemical phenomena in the epitaxial growth of semiconductor films has not yet been clarified. There is only a single report (4) of a twofold increase in the rate of germanium transport in combination with redistribution of the doping impurity when an electric field of up to 1 kV was applied between the substrate and an additional electrode, using the disproportionation reaction

$$\mathrm{Ge(solid)} + \mathrm{GeJ_4(g)} \rightleftharpoons 2\mathrm{GeJ_2(g)}.$$

However, the authors did not give a convincing explanation of the observed effect.

In order to further investigate the mechanism of transport using gas-transport reactions, we attempted to measure the e.m.f. of the system during the epitaxial growth of germanium on germanium by the small-gap method (5,6), and to determine the dependence of the transport rate on the magnitude and direction

Fig. 1. Diagram of the apparatus. 1 —quartz tube, 2 —ring-shaped heater, 3 —germanium rods

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Fig. 2. Dependence of the temperature difference in the gap (a), emf (b), and current (c) on the heater position

Figure 2: Fig. 2. Dependence of the temperature difference in the gap (a), emf (b), and current (c) on the heater position

of the electromotive force. To study these regularities, a system was chosen in which germanium transport was used in an atmosphere of hydrogen saturated with water vapor. According to literature data (^{7}), germanium transport occurs by means of the reversible reaction:

$$Ge + H_2O \rightleftharpoons GeO + H_2. \tag{1}$$

The apparatus (Fig. 1) consisted of a quartz tube into which two germanium rods 60 mm long were placed, cut from a single crystal in such a way that their end faces had the crystallographic orientation (111). The distance between the end faces, preliminarily chemically polished, was set equal to 0.3-0.8 mm. Leads for connection to the measuring–

instruments, carefully checking the quality of the ohmic contacts. On the outside of the quartz tube there was a ring-shaped resistance heater, which could be moved smoothly along the tube at a rate of 50 mm/h. The heater provided heating of a narrow zone, 10 mm wide, to 700-800°. Hydrogen, saturated with water vapor to the required concentration, was passed through the quartz tube.

Fig. 1. Diagram of the apparatus. 1 —quartz tube, 2 —ring-shaped heater, 3 —germanium rods

As the heater moved, the temperature field it produced moved over the gap between the ends of the germanium rods, changing both the temperature difference between them and their absolute temperature. Fig. 2, *a* shows the temperature difference over the gap as a function of the heater position.

Fig. 2. Dependence of the temperature difference in the gap (*a*), emf (*b*), and current (*c*) on the heater position

Fig. 3. Rate of germanium deposition as a function of heater position

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Figure 3: Fig. 3. Rate of germanium deposition as a function of heater position

Measurement of the emf and of the current arising between the germanium rods during the epitaxial growth process was carried out with a VLU-2 tube voltmeter and an F-18 Webermeter, to whose outputs self-recording instruments N-373 and PS1 were connected.

Curves *b* and *c* in Fig. 2 show the change in emf and current as a function of the heater position. Both curves are characterized by the presence of maxima and by a change in polarity at the point where the direction of the temperature difference changes. The hotter rod always had a negative charge relative to the colder one. This charge distribution is equivalent to the transfer, through the gap between the ends, of positively charged particles in the direction from the hot surface to the colder surface. It follows from this that the observed phenomenon is not associated with thermionic emission of electrons from the heated surface of germanium.

To determine the relation between the amount of substance transferred from the source to the substrate and the magnitude of the current, experiments were carried out on prolonged epitaxial deposition of germanium at a constant current value, the latter being selected on different portions of the current-strength curve. Fig. 3 shows the dependence of the transfer rate on the heater position, and Table 1 compares the amounts of transferred

substance, according to the experimental data and by calculation, based on the assumption that Faraday' s law is valid for this process.

As can be seen from Table 1, the true amount of substance transferred greatly exceeds the calculated value. This makes it possible to assume that, alongside the basic transfer mechanism expressed by reaction (1), there exists another one, which in our view is associated with the thermal dissociation of water vapor,

$$\mathrm{H_2O} \rightleftarrows \mathrm{H^+} + \mathrm{OH^-}; \tag{2}$$

and can be expressed by the following equations:

$$\mathrm{Ge} + \mathrm{OH^-} \rightleftarrows \mathrm{GeO} + \mathrm{H^+} + 2e \quad \text{(at the source)} \tag{3}$$

$$\mathrm{GeO} + 2\mathrm{H^+} \rightleftarrows \mathrm{Ge} + \mathrm{H_2O} - 2e \quad \text{(on the substrate)} \tag{4}$$

Table 1

Transfer of substance as a function of current strength in the "source –substrate" circuit

Experiment No.	Current (μA)	Amount of germanium transferred (μg/h), weighed	Amount of germanium transferred (μg/h), calculated	Ratio of weighed to calculated	Experiment No.	Current (μA)	Amount of germanium transferred (μg/h), weighed	Amount of germanium transferred (μg/h), calculated	Ratio of weighed to calculated
1*	0.06	80	2.2	36	4	0.06	320	2.2	145
2	0.13	520	4.8	110	5	0.12	850	4.5	190
3	0.01	50	0.47	120	6	0.04	240	1.5	160

* The experiment numbers correspond to the numbers of the points in Fig. 3.

Indeed, during growth the substrate potential always remained positive with respect to the source potential.

The amount of substance transferred, calculated from the presence of dissociated vapor, proved comparable with the amount calculated from Faraday' s equation.

Finally, the very fact of the appearance of an emf argues in favor of reactions (3) and (4), since free electrons do not take part in reaction (1).

It should also be noted that the emf values observed in the experiments are numerically close to the value of the ionization potential of water, equal to 12.59 V (8).

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Note: Figure translations are in progress. See original paper for figures.