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1960

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Abstract

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ADSORPTION CHANGES IN THE SURFACE CONDUCTIVITY OF GERMANIUM

(Presented by Academician A. N. Frumkin on 15 IX 1959)

An increase in the values of reverse currents passing through a p–n junction is in many cases associated with its shunting by surface conductivity ([1]). To reduce this effect, germanium crystals are subjected to etching; moreover, the etchant composition must meet the requirement of high purity, since etching mixtures are prepared on the basis of hydrofluoric and nitric acids, which, as chemical analysis shows, contain as impurities Na, Cu, Al, Zn, Mg, Mn, Fe, Cr, Pb, and other elements.

The atoms of these elements, adsorbing from the etchant onto the semiconductor surface, can cause an increase in surface conductivity. Until now, however, there had been no direct experiments showing how the surface conductivity changes upon adsorption of particular impurities. The present investigation was undertaken for this purpose.

Single-crystal n-type germanium with a resistivity of approximately 40 $\Omega \cdot$ cm was chosen as the object. Measurements of surface conductivity were carried out by the "wedge" method ([2]). Wedge-shaped specimens were cut from ingots of pure (uncompensated) germanium with a uniform (within $\pm 5\%$) distribution of resistivity along the length of the ingot.

The initial etchant consisted of HNO_3, HF, and CH_3COOH in the ratio, respectively, $3 : 2 : 1$. The acids were first subjected to double distillation, so that the total amount of impurities in each of them did not exceed $10^{-6}\%$. A definite amount of the impurity under study was introduced specially into the etching mixture. The impurity was introduced either in the form of the corresponding salt or in the form of metal filings. Etching of the wedge-shaped specimens was performed in the usual way: the temperature of the etching mixture was $\sim 100^{\circ}$, and the etching time was 30 sec. The etched specimens were washed in ion-exchange water and dried in a drying oven for 15 min at 80°.

To illustrate the results obtained, Fig. 1 presents data for a specimen etched in a pure etchant and in an etchant contaminated with iron in an amount of 0.5 wt. %. A similar effect of increased surface conductivity was also observed when impurities such as Cu, K, Cr, Ca, and Ag were introduced into the etching mixture in amounts of 0.05–1.0%.

At the same time it was found that etching in a mixture contaminated with Zn, on the contrary, reduces the surface conductivity. Such an "anomalous"

Fig. 1

Figure 1: Fig. 1

influence of zinc requires a special explanation.

However, it proved very difficult to explain this phenomenon using any simple model of electron redistribution in the adatom–substrate system. A decrease in surface conductivity was observed–

was also observed upon adsorption of Cd. It is characteristic that this phenomenon is not inherent in elements located in one and the same group of the periodic system. Thus, for example, adsorption of Ca causes an effect opposite to the action of Zn and Cd. Table 1 gives summary data on the influence on the magnitude of the surface conductivity of all the impurities studied.

Further, when Br was introduced into the etchant, the greatest change in surface conductivity was observed. Thus, etching in an etchant containing 1.0% Br introduced in atomic form lowered the surface conductivity so strongly that the ratio $\sigma_{\mathrm{p}}/\sigma_{\mathrm{po}}$ was only ~ 0.17. The introduction into the etchant of 1.0% Br in the form of KBr led to a considerably larger value of $\sigma_{\mathrm{p}}/\sigma_{\mathrm{po}}$, equal in this case to 0.5. This is apparently explained by the opposite action of K and Br atoms upon their joint adsorption.

The experiments performed show the possibility of obtaining a germanium surface with a prescribed value of surface conductivity, i.e., here we have a kind of doping of the surface with "donors" and "acceptors," carried out by means of adsorption of various impurities from the etchant.

Fig. 1. Plot of $A = \frac{I}{S} \cdot \frac{dx}{dU} = f(x)$. ($I$–current passing through the specimen, $\frac{dU}{dx}$–potential gradient), a–pure etchant, b–etchant with 0.5% Fe, S–width of the wedge-shaped specimen, σ_{po}–surface conductivity after etching in pure etchant, σ_{p}–surface conductivity after etching in contaminated etchant

Table 1

Element	Compound in the form of which the element was introduced into the etchant	Amount of element in the etchant, wt. %	$\sigma_{\mathrm{p}}/\sigma_{\mathrm{po}}$
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	1.0	1.375
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	0.5	1.00
K	KNO_3	0.355	1.5

Element	Compound in the form of which the element was introduced into the etchant	Amount of element in the etchant, wt. %	σ_p/σ_{po}
K	KNO_3	0.05	1.0
Cr	$Cr(NO_3)_3 \cdot 9H_2O$	0.5	2.5
Cr	$Cr(NO_3)_3 \cdot 9H_2O$	0.05	1.5
Cr	$Cr(NO_3)_3 \cdot 9H_2O$	0.005	1.0
Fe	Filings	0.5	1.5
Fe	Filings	0.05	1.0
Zn	$Zn(CH_3COO)_2$	1.0	0.25
Zn	$Zn(CH_3COO)_2$	0.5	0.625
Ca	$Ca(NO_3)_2 \cdot 4H_2O$	1.0	1.58
Cd	$Cd(NO_3)_2 \cdot 2H_2O$	1.0	0.75
Ag	$Ag(NO_3)$	1.0	2.0

A particular case of such surface doping is the simultaneous introduction into the etchant of impurities opposite in their action, in order to obtain a compensated surface with a very small value of σ_p.

It seems to us that the practical use of these phenomena is very promising; but for this, of course, their stability over time must be studied, it must be determined in what form the impurities are adsorbed on the crystal surface, the changes in the rate of surface recombination occurring during adsorption must be investigated, and it must be determined whether an inversion of the conductivity type of the surface layer occurs in the course of adsorption.

M. L. Ioselevich took part in the formulation and conduct of the work; the authors express their deep gratitude to her.

Received
9 IX 1959

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