ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

The Extrinsic Photoconductivity of Chalcogens in $\text{Ge}_{1-x}\text{Si}_x$ Solid Solutions

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Abstract—The effect of ~3% of silicon additive on the energy spectra of selenium and tellurium impurities in germanium is studied. The photoconductivity spectra are measured at 80 K in a spectral range from 2.5 to 5 μ m. Narrow lines corresponding to the excited states of chalcogen ions are observed against the background of the extrinsic-photoconductivity band. It is found that the spectrum of excited states is not affected by silicon at the concentration used. An increase in the energy gaps between the conduction band and impurity states of the chalcogens is detected. © 2005 Pleiades Publishing, Inc.

Tellurium and selenium act as substitutional impurities in germanium and silicon and introduce deep doubly charged donor states into the band gap. These states correspond to the neutral and ionized states of chalcogen atoms. The known energies of impurity ionization for germanium are

Te [1]: 0.095 and 0.28 eV,

Se [2]: 0.24 and 0.372 eV,

while, for silicon, we have

Te [3]: 0.199 and 0.411 eV,

Se [4]: 0.3 and 0.52 eV.

The given energies correspond to atmospheric windows in the infrared spectral region, which makes Ge:Te(Se) and Si:Te(Se) promising as materials for the fabrication of photodetectors. In $\text{Ge}_{1-x}\text{Si}_x$ solid solutions, the band gap varies as the Si fraction increases [5]; simultaneously, the impurities' ionization energy increases, which additionally makes it possible to control the photosensitivity range.

Narrow peaks corresponding to transitions to the excited states of chalcogen ions are observed against the background of conventional impurity bands in the photoconductivity spectra of germanium doped with chalcogens. It is noteworthy that a single peak with a positive polarity is observed in the spectra of the samples doped with tellurium, whereas three negative peaks correspond to the selenium impurity [6, 7]. In order to obtain data on the origin of the differences between the behavior of the chalcogen impurities, we studied the photoconductivity spectra of the Ge_{1-x}Si_x solid solutions doped with Te and Se.

We used the method of horizontal recrystallization in a graphite boat to grow single crystals of a Ge–Si alloy that had an Si content of no higher than 3% and was doped with chalcogens. Since the initial material had *p*-type conductivity and the Ga concentration was ~10¹⁵ cm⁻³, the donors were partly compensated. If the compensation factor $K \approx 0.5$, features related to the transitions of the impurity ions to an excited state were observed in the photoconductivity spectra of Ge doped with chalcogens [8]. The addition of silicon led to an increase in the ionization energy.

In Fig. 1, we show the spectral dependence of the photoeffect for $Ge_{0.98}Si_{0.02}$:Te at a temperature of 80 K (curve 2). The spectrum of a Ge:Te semiconductor without the addition of Si is also shown for comparison. It can be seen that the peak corresponding to the electron transitions from a singly charged ionized state to



Fig. 1. The photoconductivity spectra for the (1) Ge:Te and (2) $\text{Ge}_{0.98}\text{Si}_{0.02}$:Te samples. The spectra were measured at 80 K. For all the samples, the compensation factor was equal to $K \approx 0.5$.



Fig. 2. The photoconductivity spectra for the (1) Ge:Se and (2) Ge_{0.985}Si_{0.015}:Se samples. The spectra were measured at 80 K. The compensation factor was equal to $K \approx 0.5$ for all the samples. The vertical dashed and dotted straight lines indicate the energies that correspond to features in the spectra (from left to right) at hv = 353, 360, 362, 368, and 373 meV.

an excited state is shifted by 7 meV to higher energies for the sample with Si (curve 2), whereas the longwavelength edge corresponding to the electron transitions from a neutral state to the conduction band is shifted by 16 meV. The introduction of 4.5% of Si into germanium leads to an increase of 30 meV in the ionization energy and, simultaneously, to a shift of the peak by 16 meV with respect to the position of the peak in Ge:Te. Thus, the ionization energy for a neutral tellurium atom changes by 7–8 meV as a result of a 1% variation in the Si content, whereas the variation in the bonding energy amounts to 3.5 meV per 1% of Si.

In Fig. 2, we show the photoconductivity spectrum of $Ge_{0.985}Si_{0.015}$:Se at 80 K (curve 2). In contrast to tellurium, the electron transitions from the Se⁺ ion to excited states manifest themselves as three dips in the spectrum [8]. It can be seen that the introduction of Si

leads to a shift of the spectrum to shorter wavelengths and to an increase in the ionization and bonding energies by 30 meV and 7 meV, respectively (cf. curves 1 and 2); i.e., the ionization energy varies at the rate of (20 meV)/(1% Si), while the bonding energy varies at the rate of approximately (5 meV)/(1% Si).

Thus, the replacement of germanium atoms with silicon atoms does not lead to a radical transformation of the photoconductivity spectrum; rather, only quantitative changes are observed. At the same time, the rate of variation in the transition energy resulting from the introduction of Si into Ge with the selenium impurity is approximately twofold higher than in Ge with the tellurium impurity. This behavior is indicative of structural differences between the impurity centers formed by the chalcogens and can be also caused by the previously ascertained relation of the excited states of selenium ions to the L point of the conduction band and those of tellurium ions to the Γ point [2].

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