ФИЗИКА

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A Study of Tin Impurity Atoms in Amorphous Silicon

Using the Mössbauer spectroscopy method for the ^{119}Sn isotope the state of tin impurity atoms in amorphous a-Si silicon is studied. The electrical and optical properties of tin doped films of thermally spray-coated amorphous silicon have been studied. It is shown that in contrast to the crystalline silicon where tin is an electrically inactive substitution impurity, in vacuum deposited amorphous silicon it produces an acceptor band near the valence band and a fraction of the tin atoms becomes charged.

Keywords: impurity atoms, Mössbauer emission spectroscopy, amorphous silicon.

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ИССЛЕДОВАНИЕ ПРИМЕСНЫХ АТОМОВ ОЛОВА В АМОРФНОМ КРЕМНИИ

Методом мёссбауэровской спектроскопии на изотопе ^{119}Sn изучено состояние примесных атомов олова в аморфном a-Si кремнии. Исследованы электрические и оптические свойства легированных оловом пленок термически напыленного аморфного кремния. Показано, что, в отличие от кристаллического кремния, в котором олово является электрически неактивной примесью замещения, в термически напыленном аморфном кремнии оно создает полосу акцепторных состояний вблизи валентной зоны. При этом часть атомов олова оказывается в заряженном состоянии.

Ключевые слова: примесные атомы, мессбауэровская спектроскопия, аморфный кремний.

1. *Introduction*

Silicon is a typical and widely used elemental semiconductor, its properties in the crystalline state have been studied well. The interest of researchers in the amorphous modifications of silicon is therefore only natural since the comparison of the properties of the crystalline and amorphous silicon is not only of cognitive value but there is also practical significance when viewed in the context of development of cheap solar energy conversion devices [4].

While numerous investigations have been carried out on the structure of amorphous silicon, a-Si, by X-ray diffraction, the experimental radial distribution functions do not provide unambiguous information on the a-Si structure. Large potentialities in the investigation of the short-range order of amorphous materials are inherent in the Mössbauer effect [2; 3; 7]. Since silicon Möss-

bauer isotopes do not exist, we have applied the impurity Mössbauer spectroscopy, namely, the ^{119}Sn isotope that acts as an isomorphically substitutional species. It was introduced into the silicon lattice. The short-range order of a-Si is deduced from the parameters of the ^{119}Sn Mössbauer spectra [1; 5; 6].

Being the element of the group IV and forming a substitutional solid solution in silicon, tin is an "isotopic" impurity which does not produce gap states in crystalline silicon. However, it turned out that the absence of long-range order in amorphous silicon results in some unusual features in the behavior of tin in vacuum deposited amorphous silicon, so that tin can be used to control some electronic properties of this material.

2. *Experimental Method*

The tin doped amorphous silicon was obtained by vacuum evaporation from a levitated melt with crystalline silicon doped by the ^{119}Sn isotope that was used as original material. The tin concentration in the a-Si films was 5×10^{19} atoms/cm^3, the film thicknesses were 0.3 and 1.0 μm.

The temperature dependences of the electric conductivity and thermopower were measured by the two-probe technique. The optical absorption edge was determined with a DMR-4 spectrometer. The Mössbauer spectra were recorded within the temperature range from 80 to 1000 K using an electrodynamic spectrometer with a $CaSnO_3$ source. The isomer shifts are given relative to Mg_2Sn.

3. *Experimental Results*

3.1. Mössbauer data

The Mössbauer spectra of the ^{119}Sn impurity atoms in amorphous silicon represent single lines with an isomer shift close to that of the spectra of grey tin and of tin in crystalline silicon (see Fig. 1) (I.S. = 0.08 ± 0.02 mm/s, G = 1.45 ± 0.03 mm/s). Thus one may conclude that the tin impurity atoms isomorphically substitute for silicon atoms in the amorphous silicon structure forming a tetrahedral chemical bond system typical for silicon and grey tin. The increase of the tin spectrum isomer shift as one goes over from the crystalline to amorphous silicon is of interest. Since the chemical nature of the tin atom local environment is not changed by silicon amorphization, the observed increase of isomer shift can be attributed to an increase in size of the potential well where the tin impurity atom resides.

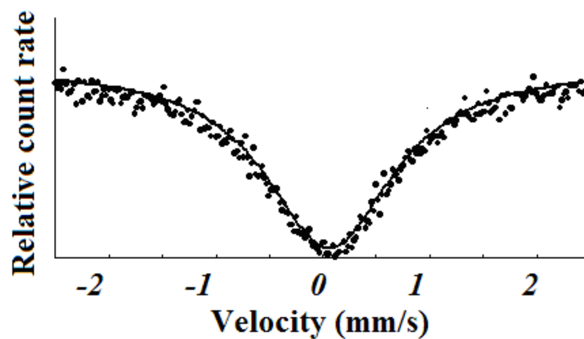

Fig. 1. Mössbauer spectra of ^{119}Sn impurity atoms in a-Si

A typical feature of the spectra of the tin impurity atoms in amorphous silicon is their broadening. There may be two reasons for this broadening:

1. Distortion of bond angles of the tin atoms with their nearest neighbors should produce broadening through unresolved quadrupole splitting. A treatment of the experimental spectra under this assumption leads to a quadrupole splitting of Δ = (0.55 ± 0.03) mm/s. This value of Δ

evidences a considerable distortion of the tetrahedral valence angles which is in agreement with the data [1] implying that the valence angle distortion in a-Si can reach 20° relative to the normal tetrahedral angle of 109°28'.

2. Fluctuations in separation from the tin atoms to their nearest neighbors should produce broadening as a result of the inhomogeneous isomer shift. In order to determine the tin atom electronic configurations responsible for the inhomogeneous isomer shift, the latter were assumed to follow a Gaussian distribution

$$W = \frac{1}{\Delta\sqrt{2\pi}} \exp\left[-\frac{(\delta_0 - \delta)^2}{2\Delta^2}\right], \quad (1)$$

where δ_0 is the average isomer shift (given in Table 1), Δ is the standard deviation. Under these conditions the shape of line is described by the expression

$$N(\mathrm{v}) = N_\infty \left\{ 1 - \varepsilon \int_{-\infty}^{\infty} \frac{\exp\left[[-\frac{(\mathrm{v}' - \mathrm{v}_0)^2}{2\Delta^2} \right]}{4\left(\frac{\mathrm{v} - \mathrm{v}'}{G}\right)^2 + 1} d\mathrm{v}' \right\}, \quad (2)$$

where v_0 and v' are the velocities corresponding to δ_0 and δ; N(v) and N_∞ are the count rates in the channels corresponding to velocities v and v_∞; ε is a parameter characterizing the amplitude of the spectrum.

The calculated and experimental spectra can be fitted by adopting $\Delta = 0.40$ mm/s. Using the isomer shift calibration of the ^{119}Sn Mössbauer spectra [2] we find that the change in the isomer shift of 0.40 mm/s should correspond to electron configuration changes for tin from $5s^{0.76}p^{2.28}$ to $5s^{1.26}p^{3.78}$, with the most probable configuration $5s^{0.98}p^{2.94}$. All these electron configurations relate to such atomic configurations where silicon atoms reside at equal separations from one another in tetrahedron vertices in the first coordination sphere of the tin atoms, the electronic configuration $5s^{0.98}p^{2.94}$ corresponding to an effective tin charge close to zero (which is a purely covalent bonding), and the configurations $5s^{0.76}p^{2.28}$ and $5s^{1.26}p^{3.78}$ corresponding to effective tin charges of +0.96 e and −1.04 e. This indicates a possibility of stabilization of charged atoms in the structure of amorphous silicon.

It should be emphasized that while the tin concentration in a-Si was 5.10^{19} atoms cm^{-3}, no lines which might be ascribed to tin associates were found in the Mössbauer spectra which indicates that the amorphization of silicon shifts the association process toward higher tin concentrations.

3.2. Electrical and optical studies

Stabilization of tin charged defects in the amorphous silicon structure should result in noticeable changes in the electronic properties of a-Si. To determine the effect of charged tin centers on the electrical and optical properties of amorphous silicon, measurements were carried out of the temperature dependences for electric conductivity σ (Fig. 2) and thermopower S (Fig. 3), and of the optical band gap E_{opt} (Fig. 4) in the undoped and tin doped amorphous silicon.

For undoped a-Si the electric conductivity can be fitted by a relationship $\sigma \sim \exp(-E/kT)$, with $E = E_1 = 0.16$ eV for 300 K < T < 400 K (region I) and $E = E_2 = 0.40$ eV for T > 400 K (region II) (see Fig. 2). Region I corresponds to hopping conduction over localized states in the mobility gap. The thermopower in this region is negative and small (see Fig. 3). Region II is charac-

terized by a drastic increase of the thermopower in absolute magnitude although it remains negative. This indicates that conduction in region II occurs over extended states in the conduction band, the quantity E_2 corresponds to the distance from the Fermi level to the mobility edge for electrons.

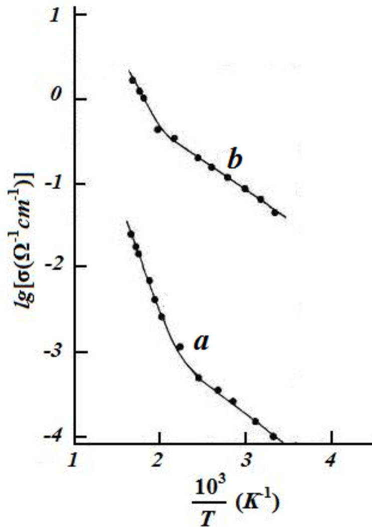

Fig. 2. Temperature dependences of the electric conductivity σ of (a) undoped and (b) tin doped amorphous silicon

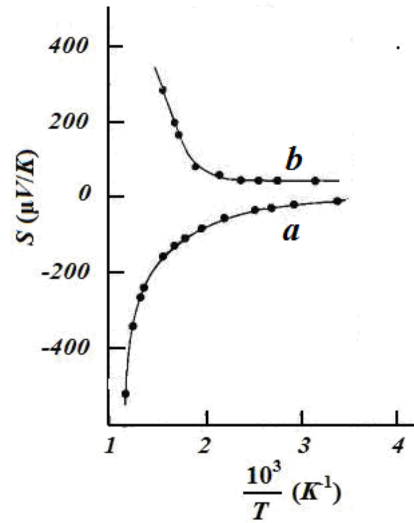

Fig. 3. Temperature dependences of the thermopower S of (a) undoped and (b) tin doped amorphous silicon

For undoped a-Si the electric conductivity can be fitted by a relationship $\sigma \sim \exp(-E/kT)$, with $E = E_1 = 0.16$ eV for 300 K < T < 400 K (region I) and $E = E_2 = 0.40$ eV for T > 400 K (region II) (see Fig. 2). Region I corresponds to hopping conduction over localized states in the mobility gap. The thermopower in this region is negative and small (see Fig. 3). Region II is characterized by a drastic increase of the thermopower in absolute magnitude although it remains negative. This indicates that conduction in region II occurs over extended states in the conduction band, the quantity E_2 corresponds to the distance from the Fermi level to the mobility edge for electrons.

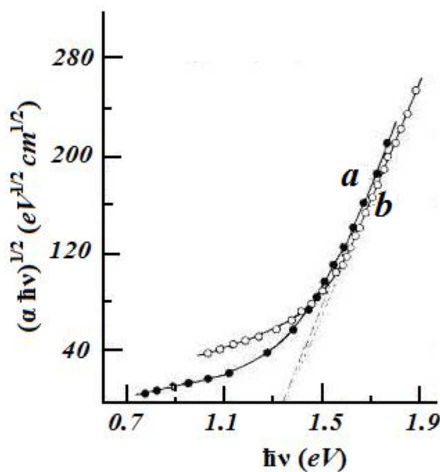

Fig. 4. Optical absorption edge of(a) undoped and (b) tin doped amorphous silicon (α — coefficient of absorption, $\hbar$ — Planck's constant, ν — frequency of the light)

Introducing tin into the structure of a-Si changes the behavior of the electric conductivity and thermopower. First, the thermopower for doped samples is positive throughout the tempera-

ture range covered (Fig. 3). Second, the electric conductivity increases substantially in magnitude (Fig. 2). Third, E_2 = 0.34 eV for doped a-Si while the magnitude of E_1 is practically unaffected by doping. It is essential that the temperature behavior of the thermopower for undoped and doped a-Si is qualitatively the same (see Fig. 3) which implies the same type of conduction in these materials. However, for doped samples conduction in region II occurs over the valence band, the band of localized states lying at 0.34 eV from the valence band mobility edge. Note that doping does not change the band gap of a-Si (see Fig. 4) and, hence, the observed changes in the conductivity and thermopower cannot be accounted for by shifts of the mobility edges.

4. *Conclusion*

The introduction of tin impurity atoms, rather than changing drastically the band structure of amorphous silicon, results only in the formation of a band of localized states near the valence band to which the Fermi level is pinned. Tin in crystalline silicon is known to behave as an isoelectronic neutral impurity, whereas in amorphous silicon its introduction produces a noticeable change in the magnitude of the conductivity and a change of the major carrier type. This difference in tin behavior in the two silicon modifications can be attributed to a difference in the electronic structure of the tin impurity centers in amorphous and crystalline silicon, namely, while all tin atoms in crystalline silicon form a neutral tetrahedral chemical bond system, some of tin atoms in amorphous silicon, besides such atoms, reside in the charged state.

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Zinc Impurity Atoms in GaP, GaAs, and GaSb Examined with Mössbauer Spectroscopy

Mössbauer spectra of ^{67}Ga(^{67}Zn) and ^{67}Cu(^{67}Zn) impurity atoms in the bulk of GaP, GaAs, and GaSb samples correspond to isolated zinc centers at Ga sites. The observed shift of the spectral centers of gravity to higher positive velocities at the transition from p- to n-type samples corresponds to the recharging of a shallow zinc impurity center. Mössbauer spectra of ^{67}Cu(^{67}Zn) impurities at the surface of samples represent a superposition of spectra corresponding to isolated zinc centers at gallium sites with those corresponding to zinc associates with an arsenic vacancy.

Keywords: Mössbauer spectroscopy, impurity atoms, zinc.

А. В. Николаева

ПРИМЕСНЫЕ АТОМЫ ЦИНКА В GaP, GaAs И GaSb, ИЗУЧЕННЫЕ МЕТОДОМ МЁССБАУЭРОВСКОЙ СПЕКТРОСКОПИИ

Мессбауэровские спектры примесных атомов ^{67}Ga(^{67}Zn) и ^{67}Cu(^{67}Zn) в объемной части образцов GaP, GaAs и GaSb отвечают изолированным центрам цинка в узлах галлия. Наблюдается сдвиг центра тяжести спектров в область положительных скоростей при переходе от дырочных к электронным образцам, и это соответствует перезарядке мелкого примесного центра цинка. Мессбауэровские спектры примесных атомов ^{67}Cu(^{67}Zn) в приповерхностной области образцов представляют собой суперпозицию спектров, отвечающих изолированным центрам цинка в узлах галлия, и спектров, отвечающих ассоциатам цинка с вакансией мышьяка.

Ключевые слова: мессбауэровская спектроскопия, примесные атомы, цинк.

It is well known that a zinc impurity in III-V compounds forms shallow acceptor levels (0.02–0.04 eV above the valence band edge) [6]. A study of zinc impurity atoms in GaP, GaAs, and GaSb using emission Mössbauer spectroscopy of the ^{67}Ga(^{67}Zn) isotope opens the way to revealing the effect of electrical activity of “daughter” atoms (with the evident inactivity of “parent” atoms) on the Mössbauer spectral parameters of the ^{67}Zn probe, whereas the relevant spectra of the ^{67}Cu(^{67}Zn) isotope make possible the study of a similar effect for both daughter and parent atoms [1–5; 7]. According to [6], a copper impurity forms shallow donor levels in III-V compounds (in GaAs, they lie at ~ 0.07 eV below the conduction band edge) and deep two-electron acceptor levels (~ 0.14 and 0.44 eV above the valence band edge in GaAs).