

## Diffusion of Silver in TiSe<sub>2</sub> Single Crystals<sup>1</sup>

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**Abstract**—Diffusion of deposited silver through the surface of TiSe<sub>2</sub> single crystals has been investigated. It is found that diffusion occurs only near lattice defects. The X-ray photoelectron spectra of TiSe<sub>2</sub> single crystals with in situ deposited silver have been studied. It is found that, upon annealing in the spectrometer chamber, silver does not form chemical bonds with the host lattice.

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Titanium diselenide and ditelluride, intercalated with silver, demonstrate interesting physical properties, in particular, the presence of a temperature range of charge carrier localization, limited from above and below [1, 2]. Such unusual behavior is related to the formation of covalent centers in this temperature range and, therefore, transformation of the electronic structure. Detailed investigation of this phenomenon should be performed on single crystals. However, at elevated temperatures, it is the phase with a spinel structure that is stable in these materials, rather than the layered phase of interest [3]. This circumstance initiated the search for methods of obtaining Ag<sub>x</sub>TiX<sub>2</sub> (X = Se, Te) single crystals without heating. A natural version is the diffusive saturation of TiX<sub>2</sub> single crystals with silver at temperatures below the transition point to the spinel phase.

To implement this technique, metallic silver was deposited at room temperature on the basal plane of TiSe<sub>2</sub> crystals, after which the crystals were annealed at temperatures from 500 to 800°C for a week. The films obtained turned out to be too thin for X-ray diffraction analysis; therefore, the degree of silver dissolution was mainly monitored by optical microscopy on a MIM-8M microscope. Photo imaging of the crystal surface was performed with a magnification of 100. Then, panoramic surface images were constructed using the Adobe Photoshop package. To obtain information about silver penetration into crystals, the latter were exfoliated using a scotch. Analysis of the panoramic images of TiSe<sub>2</sub> single crystals coated with silver films and annealed at different temperatures showed that silver was dissolved only at annealing temperatures not lower than 900°C. At lower annealing temperatures, an

Ag<sub>2</sub>Se film was formed on the crystal surface, which had a significant thickness. Due to the difference in the volumes of Ag<sub>2</sub>Se and TiSe<sub>2</sub>, the film was warped, and its contact with the crystal surface became pointlike. It is likely that, due to this circumstance, pronounced dissolution of silver in TiSe<sub>2</sub> was not observed even at such long-term annealings as two months. Heating of crystals coated by a thick Ag<sub>2</sub>Se film to 900°C led to the complete film elimination and dissolution of silver in crystals. Thus, it was established that, at temperatures up to 500°C, Ag<sub>2</sub>Se is thermodynamically more stable than Ag<sub>x</sub>TiSe<sub>2</sub>, whereas at 900°C the situation becomes opposite. It is likely that such behavior can be due to the higher entropy of the silver subsystem in Ag<sub>x</sub>TiSe<sub>2</sub> in comparison with Ag<sub>2</sub>Se, which is explained by the much higher concentration of sites accessible for occupation by silver in TiSe<sub>2</sub> in comparison with Ag<sub>2</sub>Se.

At low-temperature annealings, silver dissolution was observed only near the crystal structure defects, which can be interpreted as screw dislocation outcrops, growth steps, and the crystal edge. In the areas far from these defects, the silver film retained even after annealing at 500°C for two months.

The spectroscopic analysis was performed on an ESCALAB-5 spectrometer at the Institute of Solid-State Physics (Chernogolovka, Russia). Deposition was performed in the working chamber: two silver monolayers were evaporated on a previously cleaved surface of a single crystal. Directly after deposition, we measured X-ray photoelectron spectra, low-energy electron diffraction (LEED) patterns (which made it possible to estimate the surface purity and the crystal structure type), and electron energy loss spectra. Then the crystal was annealed in a preparation chamber at 200°C for 2 h. After the annealing, the crystal was returned to the working chamber and

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**Table 1.** Comparison of the relative intensities of Se, Ti, and Ag spectral lines

Pure TiSe <sub>2</sub>	Before annealing	After annealing
$\frac{\text{Se } 3p_{3/2}}{\text{Ti } 2p_{3/2}} = 1.03$	$\frac{\text{Se } 3p_{3/2}}{\text{Ti } 2p_{3/2}} = 0.97$	$\frac{\text{Se } 3p_{3/2}}{\text{Ti } 2p_{3/2}} = 0.99$
–	$\frac{\text{Ag } 3d_{5/2}}{\text{Ti } 2p_{3/2}} = 1.19$	$\frac{\text{Ag } 3d_{5/2}}{\text{Ti } 2p_{3/2}} = 1.14$

the entire set of the spectral measurements was repeated.

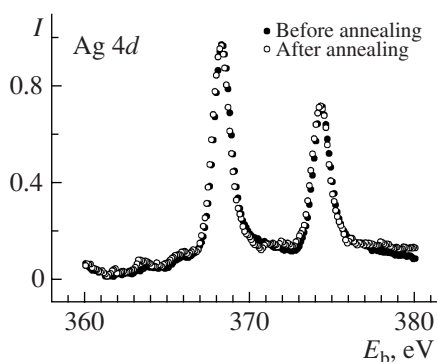
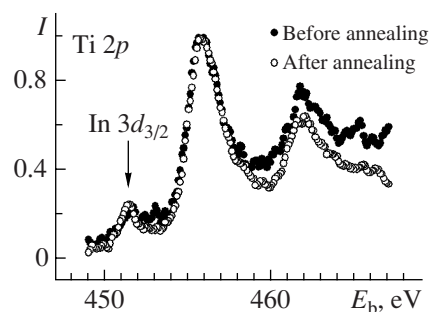
Analysis of the LEED patterns shows that silver deposition leads to blurring of diffraction peaks. Additional peaks do not arise even after annealing; this fact suggests silver disordering. Silver penetration into the crystal can be estimated from the change in the relative intensities of selenium, titanium, and silver spectral lines (Table 1). It can be seen that the relative peak intensity Ag/Ti changes after annealing. This fact indicates silver diffusion into the sample. However, chemical bonds are not formed in this case on the crystal surface. Formation of chemical bonds manifests itself in spectral shifts. No such shifts (exceeding the measurement error) were found in our experiment. This means that the annealing temperature and/or time were insufficient to form chemical bonds between silver and the crystal lattice. The positions of line centroids are listed in Table 2. The X-ray photoelectron spectra of TiSe<sub>2</sub> with deposited silver are shown in Figs. 1–3. The valence-band spectrum, containing additional lines,

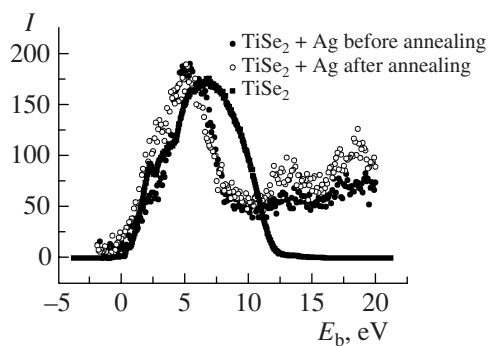
**Table 2.** Positions of the spectral lines (eV) for pure TiSe<sub>2</sub> and TiSe<sub>2</sub> with deposited silver before and after annealing

Line	Element	Pure TiSe <sub>2</sub>	Before annealing	After annealing
Ti 2p <sub>3/2</sub>		455.6	455.6	455.7
Ti 2p <sub>1/2</sub>		461.9	461.7	462.0
Se 3p <sub>3/2</sub>		159.6	159.6	159.5
Se 3p <sub>1/2</sub>		165.3	165.7	165.6
Se 3d		53.2	53.4	53.5
Ag 3d <sub>5/2</sub>		–	368.3	368.2
Ag 3d <sub>3/2</sub>		–	374.3	374.2

is of greatest interest. These lines are indicative of silver diffusion into the sample (Fig. 3). Previously, Starnberg [4, 5] performed spectroscopic analysis of TiSe<sub>2</sub> and TiS<sub>2</sub> crystals with alkali metal and silver films deposited on their surface. In this case, changes in the spectral line positions were observed. On the basis of this fact, it was concluded that metal diffuses into the sample and a chemical bond is formed between the intercalant and host. The experiment was performed at a temperature not higher than 300°C. The results of our investigation indicate that such a temperature is, apparently, insufficient to form chemical bonds. Annealing leads to the formation of the Me<sub>2</sub>X chemical compound (Me and X are deposited metal and chalcogen, respectively) on the surface, and the spectral lines are shifted due to the lattice enrichment with excess titanium as a result of the chalcogen loss.

Thus, it is shown that silver on the crystal surface behaves differently at different annealing temperatures. Diffusion of silver near lattice defects

**Fig. 1.** Ag 4d line (*I* is the intensity in relative units, *E<sub>b</sub>* is the binding energy).**Fig. 2.** Ti 2p line (*I* is the intensity in relative units, *E<sub>b</sub>* is the binding energy).



**Fig. 3.** Valence-band spectrum ( $I$  is the intensity in absolute units,  $E_b$  is the binding energy).

makes it possible to use this technique for detecting screw dislocation outcrops on the crystal surface.

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