Contributed paper

Radiation-induced paramagnetic centers in amorphous chalcogenide semiconductors

OLEG I. SHPOTYUK[1, 2*], MYKOLA M. VAKIV[2], ANDRII O. MATKOVSKII[2], ANDRII P. KOVALSKII[2]

[1]Scientific Research Institute of Materials, Lviv, Ukraine
[2]Physics Institute, Pedagogical University, Częstochowa, Poland

The microstructural mechanism of radiation-induced processes in amorphous chalcogenide semiconductors is established using electron spin resonance (ESR) technique. It is shown that investigated low-temperature ($T < 100K$) radiation-induced structural transformations are accompanied by chemical bonds breaking and switching. Paramagnetic S_2=As· As–S· and As–As· centers (unpaired electron is denoted by point) are formed.

1. Introduction

The electron spin resonance (ESR) method was firstly applied with the purpose of an experimental identification of chemical bond destruction processes induced in amorphous chalcogenide layers by absorbed light beam [1]. In this paper we shall try to use this technique for investigation of low-temperature paramagnetic defects in amorphous chalcogenide semiconductors (As_2S_3-type) stimulated by γ-radiation.

The samples of vitreous υ–As_2S_3 were synthesized from pure constituents in evacuated quartz ampoules [2].

The γ-irradiation was carried out with the ^{60}Co isotope (1.25 MeV) at 77 K, a dose rate of 25 *Gy/s* and absorbed dose of 10 *Gy*.

ESR measurements were carried out using υ-As_2S_3 powder. ESR spectra were obtained at 77 K in a nitrogen gas flow with a standard Varian E-9 X-band bridge spectrometer.

2. Experimental results

An ESR signal is not observed in non-irradiated or thermally annealed at T = 420-450 K samples of υ-As_2S_3. But it is distinctly displayed in samples γ-irradiated and studied at temperatures less than 100 K. The obtained signal is shown in Fig. 1. Some types of paramagnetic centers in the structure of υ-As_2S_3 correspond to it.

Slight bends in the central part of the ESR signal defined as components 4 and 7 (Fig.1) are typical for freshly quenched vitreous samples. It is established that the *g*-factor of this singlet signal is equal to 1.970 and its width is ΔB = 140 Gs. The obtained ESR components are bleached at T > 150 K and are not observed in the second and all following γ-treatment cycles. The ESR signal containing components 2 and 8 (g_2= 2.183, g_8= 1.847, $\Delta B_2 = \Delta B_8 < 1$ Gs) is bleached at T > 160 K. Both above-mentioned signals do not appear in γ-ir-

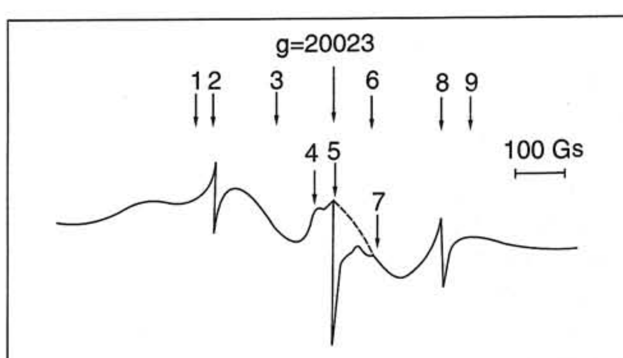

Fig.1. ESR spectrum of υ-As_2S_3 γ-irradiated with 10^5 *Gy* dose.

* corresponding author: Oleg I. Shpotyuk, Scientific Research Institute of Materials, 202 Stryjska Str., Lviv 290031, Ukraine

radiated samples at repeated cooling. The ESR component 5 in Fig. 1 (g_5= 2.002, ΔB_5 = 7.5 Gs) is shown also at temperatures near 300 K, but its definition under these conditions is difficult because of the high noise level.

A detailed study of temperature and composition dependences for ESR components 1, 3, 6, and 9 shows that they correspond to paramagnetic centers formed mutually by γ-irradiation (Fig.1). The total width of this signal is near 1000 Gs and its characteristics are the following: g_3 = 2.065, ΔB_3 = 90 G, g_6 = 1.950, ΔB_6 = 110 Gs (an exact identification of components 1 and 9 appearing as slight and broad bends at the ends of the whole ESR signal is impossible under these conditions). This signal is bleached at T > 210 K.

3. Discussion of results

The identification of low-temperature paramagnetic centers induced by γ-irradiation will be made taking into account previous results on photoinduced ESR [1, 4].

The four-component signal including ESR lines 1, 3, 6, and 9 (see Fig. 1) due to its spectroscopic characteristics, splitting parameters, composition and temperature dependences is related to paramagnetic As-S· and S_2=As· defects (the unpaired spin is marked by a dot). Both defects appear as the result of γ-treatment when the heteropolar As-S bond is destroyed. The unpaired electron is localized on a *p*-like orbital. However, if photoinduced ESR of these defects is associated with a formation of new paramagnetic centers on existing diamagnetic ones, γ-irradiation stimulates the additional paramagnetic centers formation due to chemical bonds destruction. It leads to a higher localization degree of radiation defects in comparison with photoinduced ones. Accordingly, the structure of the ESR signal of γ-irradiated samples is more distinct.

The singlet ESR signal with g = 1.970 and ΔB = = 140 Gs observed in freshly quenched υ-As_2S_3 after radiation treatment was previously identified in light-irradiated thin films as the signal of an unpaired electron localized at an arsenic atom near a disturbed As-As bond [4]. This fact indicates that a certain small concentration of "wrong" homopolar bonds is kept in vitreous samples.

The doublet signal with resonance splitting A = 502 Gs, containing the two asymmetric lines 2 and 8 (Fig.1) which are mutually inverted, corresponds to the ESR signal of hydrogen atoms (g_{av}= 2.015, $\Delta B_2 = \Delta B_8$ < 1 Gs). The same signal was earlier obtained in silica [5]. The source of hydrogen atoms may be impure complexes S-H and As-OH as well as H_2O molecules adsorbed during samples preparation or γ-treatment processes.

Sharply defined ESR signal 5 is connected with hole-like paramagnetic centers having an unpaired electron localized at impurity ions of Fe or O [6]. The latter version is more probable as the concentration of iron in the studied υ-As_2S_3 does not exceed 10^{-4}%, while oxygen atoms in the form of As_4O_6, SO_2 and As-O-As complexes are usually present in all samples obtained by direct synthesis.

As was shown previously [7-10], observed changes of physical properties of amorphous chalcogenide semiconductors stimulated by high-temperature (T = 300 K) radiation treatment are explained by diamagnetic defects formation processes. These defects are coordination centers formed as products of one chemical bond destruction and another bond appearance (destruction - polymerization transformations). Hence we may consider the whole process of radiation-induced defects formation in υ-As_2S_3 at the stage of both initial paramagnetic and diamagnetic centers creation.

4. Conclusions

The existence of several types of paramagnetic defects in γ-irradiated υ-As_2S_3 at low temperatures makes one think that the process of radiation-induced transformations is taking place in two stages. The paramagnetic centers are formed in the first stage as a result of bonds destruction. They are stable at T < 100 K, and are transformed into diamagnetic or chemical bonds with host and impurity atoms, in the second stage (T = 300 K).

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