Chalcogenide Letters Vol. 7, No. 9, September 2010, p. 559 - 563

AC CONDUCTIVITY OF CdSSe-DOPED BOROSILICATE GLASSES

R.JANELIDZE[a], O.BAKRADZE[a], O.GOGOLIN[a*], E.TSITSISHVILI[a],
C. KLINGSHIRN[b]
[a]*Institute for Cybernetics, S.Euli 5, 0186 Tbilisi, Georgian Republic.*
[b]*Institute for Applied Physics, Karlsruhe Institute of Technology (KIT)*
W. Gaede Straße 1, 76133 Karlsruhe, Germany

We report measurements of dynamic (ac) electrical conductivity in borosilicate glasses doped with the semiconductors CdS_xSe_{1-x} and AgI in a wide range of frequencies and temperatures. The concentrations of homogenously dissolved dopants are governed by the heat treatment conditions of the glass samples leading to a creation of CdSSe and AgI nanocrystals. The ac conductivity rises with increasing average size of the CdSSe nanocrystals, in contrast to the case of the metal halide doped borosilicate glasses.

(Received September 2, 2010; accepted September 22, 2010)

Keywords: Glass, Chalcogenide dopants, Ionic conductivity, Nanocrystals.

1. Introduction

The doped borosilicate glasses have been used for many years to prepare commercially available colored glass edge filters [1]. The borosilicate glasses serve also as a host network structure for embedding of ensembles of semiconductor nano crystals (NCs) - quantum dots and rods. See e.g. [2-4] and references therein. Solid phase precipitation of semiconductor components in borosilicate glass is –besides precipitation from solutions- one of the best known and widely used preparation routes of such objects [1-5]. The push to study such systems has been the understanding of fundamental physics of systems of reduced dimensionality and low-dimensional confinement but also the development of an understanding of the basic questions of potential applications in communication or computing systems [6]. For both the fundamental study and application it is necessary to gain understanding and control over the growth process and the properties of large ensembles of NCs. The growth process of NCs in turn is determined by the duration and temperature of the heat treatment and depends also on a composition and properties of a host network structure [5, 7-10].

Usually the glass constituents consist of two main components, the network former and the network modifier ions [7]. In the case of borosilicate glass, B_2O_3 and SiO_2 are strong glass-formers, whereas the metal oxides serve usually as modifiers. The latter are added to achieve the appropriate conditions for a successful formation of the semiconductor NCs, since they cause a reduction of the glass melting point and viscosity and enhance the diffusion velocity of dopants. Besides, modifiers lead to a drastic enhancement of the ionic conductivity associated with a high mobility of the metallic M^+ ions even at small concentrations [7].

In this report we study the absorption spectra of CdS_xSe_{1-x}-doped borosilicate glasses and the electrical properties of them prepared under different conditions from the case of a full solution of dopants in the glass matrix to the case of their complete incorporation into NCs. The results are compared to data from AgI-doped glasses**.** Our principle tool of investigation is the measurement of the dynamic electrical conductivity in a wide range of frequencies and temperature. These studies are complemented by optical absorption measurements and the TEM investigations.

2. Experimental procedures, results and discussion

The CdS_xSe_{1-x}-doped borosilicate glass samples examined in the present studies were prepared by a technique similar to the ones described in Refs. [5, 8, 9]. The butch (SiO_2-B_2O_3-ZnO-K_2O-Na_2O + 0,86wt% of CdS, and 0,34 wt% of Se) was molten at 1300°C for 2 hours in a furnace and was then rapidly quenched to room temperature resulting in clear colorless glass sheets. Also undoped glass of the same composition was prepared. To produce the NCs, the obtained glass ingot with homogenously dissolved dopants was cut into several parts which were annealed in a furnace at temperatures ranging from 500C° to 700C° for several hours. The samples (0.05 cm thick and 2 cm^2 square) were cut from the ingots for the various measurements. Below we focus on 5 specific samples labeled S_i ($_i$ = 1 - 5). Sample S_1 is a virgin host network structure, i.e., it does not contain any dopants. In sample S_2 the dopants are homogenously dissolved in a glass matrix. In the last tree samples S_3, S_4, and S_5 dopants are partially incorporated to NC's. The TEM examinations of these samples show a nearly spherical shape of NCs with an average radius of 2 nm and 6 nm in samples S_3 and S_4, respectively, whereas a rode-like shape with an aspect ratio as large as 1:3.5 is typical for NCs in sample S_5 **(**see insets in Fig.1**).**

The optical-absorption measurements were carried out at room temperature on an AvaSpec-2048 spectrometer in the photon energy range from 1.5 eV to 2.7 eV. The obtained absorption spectra are shown in Fig.1, where the numbering of curves refers to the ones for the samples.

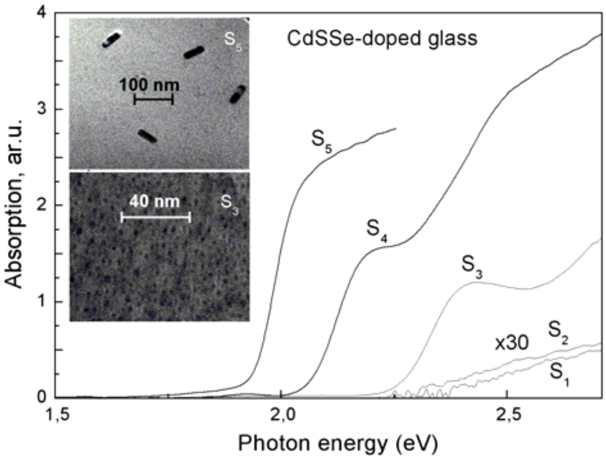

Fig.1. Absorption spectra for glass samples S_1 to S_5. Lower and upper inset: TEM image for sample S_3 and S_5, respectively.

For samples S_1 and S_2 absorption is very weak in the studied energy range and rises slowly and monotonically with increasing photon energy**.** The absorption spectra for the annealed samples S_3 and S_4 exhibit the characteristic blue shifts (with respect to the bulk band gap E_g) and show the pronounced peaks specific for the excitonic quantum confined states [5,10]. The absorption spectrum for sample S_5, which contains the large, rod-like NCs (see upper inset in Fig.1), displays a very weak confinement only. The absorption spectrum with an onset around 1.85eV is close to the one for the $CdS_{1-x}Se_x$ bulk crystal with x = 0.76 [11].

For all five samples, the electrical conductivity was measured in a frequency range from 10Hz to10^4 Hz. The silver electrodes were deposited on both surfaces of samples by vacuum evaporation and electrical measurements were performed using the selective nanovoltmeter UNIPAN 237. For the considered frequency range, the conductivity follows the empirical relation $\sigma(\omega) = A\,\omega^s$ [12], where the frequency exponent s (s < 1) is the same for all studied samples. The constant A, however, slightly differs from sample to sample. For the sake of clearness, in Fig.2 the obtained dependence is shown in more narrow range for frequencies in between 400 Hz and 1000 Hz at room temperature**.** To draw a conclusion on the character of the conductivity, we measured, additionally, the dynamic conductivity at different temperatures. As an illustration, the obtained temperature dependence up to 700 K is shown in Fig.3 for S_3 and S_5 at the frequency of 100 Hz. The other samples exhibit a similar dependence. These Arrhenius plots for the conductivities reveal activation energies of E_a = 0.74 eV and E_a = 0.57 eV for S_3 and S_5, respectively, i.e., the activation energy in sample S_3 containing dissolved dopant is larger than the one in sample S_5 where (almost) all dopants are incorporated in the NCs.

Fig.2 presents our main result: the conductivity changes from sample to sample in the considered frequency interval. The largest values of the conductivity are observed in undoped sample S_1 and also in S_5 which contains the largest CdSSe NC's. For these two samples the magnitudes of the conductivity are very close. This fact indicates that in S_5 almost the total amount of dopants is incorporated in the NCs. When an average size of the NC's decreases, the conductivity is reduced, too, and reaches the smallest values in sample S_2, which, as we recall, has undergone no heat treatment, so that it contains no NCs, but only the homogenously dissolved dopants.

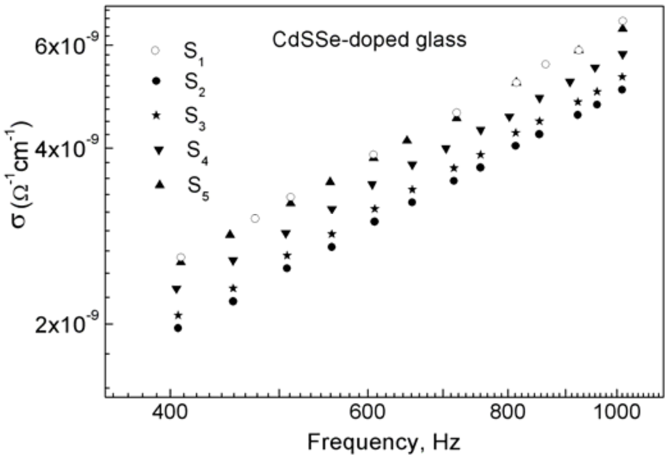

Fig.2 The frequency dependence of ac conductivity for virgin glass sample S_1 ,the homogenous glass sample S_2 , and the heat treated samples S_3, S_4, and S_5; see text .

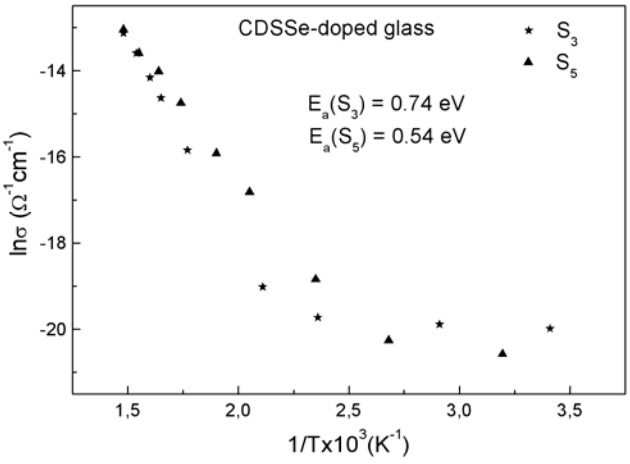

Fig.3 Arrhenius plot of ac conductivity for samples S_3 and S_5 at 100 Hz.

The obtained results indicate that the electrical conductivity of CdS_xSe_{1-x}-doped borosilicate glasses decreases remarkably with an increase of a concentration of dopants which are homogeneously dissolved in a glass. Consequently, one can conclude that the conductivity is sensitive to a creation and growth stage of the NC's in a glass matrix. Such findings can be explained in terms of a doping effect on the ionic conductivity realized in the borosilicate glasses. Indeed, the observed dependence of the conductivity on the NC (average) size can be viewed as a dependence on a concentration of dopants still dissolved in a glass matrix. (Recall that the samples were prepared from the one glass ingot, so that the initial dopant concentration is the same for all samples.) The larger are NCs the less concentration of such dopants remains. The ionic conductivity of glasses has common structural characteristic that includes a highly ordered framework complemented by a disordered interstitial "sublattice" with a number of equivalent sites greater than the number of available (randomly distributed) ions to fill them [13]. The electrical conductivity of the borosilicate glasses is determined mainly by the concentration and mobility of the metallic Na^+ ions serving as the network modifiers [12]. The Cd, S and Se dopants homogeneously dissolved in a glass as molecules and atoms during the melting process fill partially the available sites of the interstitial sublattice reducing effectively the mobility of the Na^+ ions. Consequently, the conductivity of CdS_xSe_{1-x}- doped glass (sample S_2) becomes suppressed as compared to a virgin glass (sample S_1). Such a change of the conductivity is, evidently, the stronger the higher a concentration of dopants is. Since in the annealed samples some amount of dopants is incorporated into NCs, the actual concentration of still dissolved dopants is now lower than the initial one in a homogenous, unannealed sample S_2. As a result, the conductivity in samples S_3 - S_5 is larger than in S_2. This tendency is amplified with an increase of the NCs sizes and an almost total restoration of the conductivity is achieved for sample S_5 containing the large rod-like particles, the sizes of which remain unchanged under further heat treatment.

To support the above explanation, we studied additionally the ac conductivity in AgI-doped borosilicate glasses. As is well known, the compound AgI dissolves in a glass as I^- and Ag^+ ions and the Ag^+ ions contribute essentially to the electrical conductivity [14]. Consequently, for the conductivity now one can expect the opposite trend as compared to the chalcogenide-doped glasses. We prepared the AgI –doped homogenous sample (A_1) and two annealed samples containing NCs (for the growth details see Ref. [8]) with an average radius of 2.3 nm (A_2) and 7.5 nm (A_3), respectively. The corresponding ac conductivities at room temperature are shown in Fig.4. In this figure one can seen that now the conductivity is maximal for the homogenous sample and reduces for the annealed samples in which the Ag^+ and I^- ions are partially incorporated to the NC's. The larger are NCs, the lower is now the conductivity. Similar results were previously reported for the

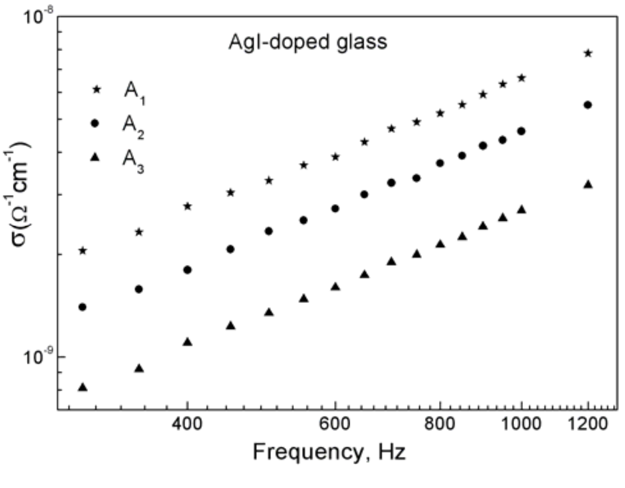

Fig.4 The frequency dependence of ac conductivity for homogenously doped sample A_1, and samples A_2 and A_3 containing nanocrystals with an average radius of 2.3 nm and 7.5 nm respectively

CuBr- and CuCl- doped borosilicate glasses [15,16]. Hence, the electrical conductivity of glass network contains information on the creation and growth of the semiconductor NCs and the conductivity measurements may serve as a method for a preliminary characterization of samples.

3. Conclusions

We have presented measurements of the dynamic electrical conductivity in (i) CdS_xSe_{1-x}-doped borosilicate glasses and (ii) in the glasses network structures containing CdS_xSe_{1-x} nano crystals of different average radii. In both cases, the frequency and temperature dependence of the conductivity was examined. Similar studies were carried out for the AgI – doped glasses.

Our measurements show that magnitude of the electrical conductivity exhibits a systematic dependence on a (average) size of NCs in a glass matrix, i.e. on the remaining concentration of dopants still dissolved in the glass matrix. For CdS_xSe_{1-x}- doped glasses, the conductivity decreases with a decrease of the NC size due to a suppression of the metallic ion (Na^+) mobility by the dopants. It contrasts thus the results for the AgI - doped glasses, where the conductivity decreases with a rise of the NC's size due to a high mobility of the Ag^+ ions. We conclude that the electrical conductivity of glass network contains information on the nucleation and growth of the semiconductor NCs and the conductivity measurements may serve as a method for a preliminary characterization of the glass network nanostructure samples.

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