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Photoelectrical characterization of nanocrystalline $AgBiS_2$ thin films

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The photoelectric properties of chemically produced nanostructured $AgBiS_2$ thin films are investigated. Atomic force microscopy is used to prove the nanocrystalline structure of the films, and a value of ~ 10 nm is obtained as an upper limit for the average grain size. The temperature dependences of the photocurrent measured in the range 77 – 390 K do not display high photosensitivity at low temperatures. This observation is related to a high density of fast recombination centers created at the interfaces between the nanocrystals. Persistent photoconductivity is measured at low-temperatures after turning off the light, and a high voltage polarization is observed on light illumination of the films. Both effects are related to trapping of photoexcited carriers in deep defect states, and are considered as responsible for the rather low value (< 0.5) of the exponent in the photocurrent intensity dependence. Constant photocurrent method measurements, carried out at energies higher than the optical band gap, reveal fine structure in the absorption spectra of the films, which could be assigned to higher excitons in $AgBiS_2$ quantum dots, and be considered as an indication of a narrow size distribution of the nanocrystals in the layers.

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1. Introduction

The important role of low-dimensional semiconductor materials in contemporary science and technology arises from their remarkable size-dependent optical properties and electronic structure [1-5]. In addition to the fundamental interest in nanosized materials, the new physical properties of low-dimensional semiconductors allow their wide application in electronics, optoelectronics, non-linear optical devices etc. [6]

Frequently, wet chemical deposition techniques are used for the preparation of thin films, because of their ability to produce nanoparticles with uniform shapes and narrow size distributions [7]. They offer cheap ways for the production of nanocrystalline thin films, when there is no requirement for ultra high purity of the layers prepared. The electrical and photoelectrical properties of such films are very sensitive to the grain size, as well as the defects in the grains and at the interfaces between them. Information about these properties is important for applications in electronics and optoelectronics.

The interest in the $AgBiS_2$ ternary semiconductor is motivated by the fact that it belongs to the group I-V-VI materials, which are used in the production of linear and nonlinear optoelectronic and thermoelectric devices, as well as in optical recording media [8,9]. The crystallographic and thermodynamic properties of bulk $AgBiS_2$ have mainly been investigated [10,11]. To the best of our knowledge, up to now no other group has synthesized this semiconductor in thin film nanocrystalline form.

In this study, nanostructured $AgBiS_2$ thin films produced by chemical deposition are investigated. Atomic force microscopy proves the nanocrystal film structure. The spectral and temperature dependences of the photocurrent in these films are measured. Based on the temperature-dependent photocurrent data, assumptions are made concerning the density and spatial dispersion of fast recombination centers. Moreover, fine structure is seen in the absorption spectra of the films, which is discussed in terms of quantum-size effects in the electronic structure of $AgBiS_2$ quantum dots.

2. Experimental details

Thin films of $AgBiS_2$ were synthesized using chemical deposition. The reaction system had the components: silver nitrate, bismuth nitrate and sodium thiosulfate. In order to avoid precipitation of $BiONO_3$, bismuth (III) nitrate was dissolved in a solution of nitric acid (c (HNO_3) = 2 mol/dm^3). A classical optimization of the experimental conditions was performed, aiming at the preparation of nanostructured material with a good photoresponse.

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The best photoelectrical properties of the layers were achieved with initial concentrations of both $AgNO_3$ and $Bi(NO_3)_3$ solutions of 0.1 mol/dm^3, initial concentration of $Na_2S_2O_3$ solution of 1 mol/dm^3, keeping the volume ratio of these three species as 1:1:1. More details on the preparation procedure can be found in [12].

The surface morphology of the layers was studied by a NanoScan atomic force microscope (AFM), using the tapping mode. Arrays of 512 x 512 pixels from 5.2 x 5.2 μm^2 area scans were taken.

Photocurrent measurements were performed using melted In contacts and applying a field of 100 V/cm. Temperature photocurrent dependences were obtained in the range 77 – 390 K, by a Keithley 6487 Picoammeter under illumination with white light (400 - 750 nm, ~ 30 mW/cm^2).

As is known ([13] and references therein), the Constant Photocurrent Method (CPM) allows precise exploration of the absorption spectrum of thin films, and thus conclusions about size induced changes in the electronic structure of photoconductive nanocrystalline materials. Therefore, CPM measurements were carried out at room temperature to study the optical absorption of the $AgBiS_2$ layers. The samples were illuminated with chopped monochromatic light (2 Hz) from an MDR 2 diffraction grating monochromator with a resolution of 2 nm/mm.

3. Results and discussion

AFM studies of the surface morphology of as-deposited films were carried out, in order to make an estimation of the grain size.

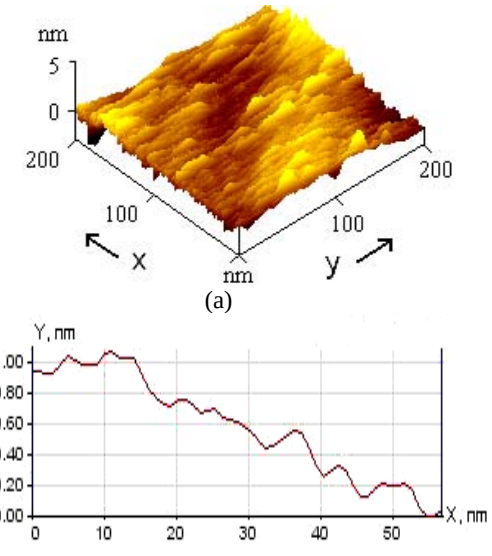

Fig. 1. (a) Three-dimensional AFM image of the surface of an as-deposited $AgBiS_2$ thin film; (b) surface relief along an line parallel to the y-axis.

Fig. 1(a) shows a three-dimensional image of an $AgBiS_2$ thin film. Large scale fluctuations are seen, having lateral sizes of ~ 50 nm and vertical amplitudes below 10 nm. Additionally, a fine structure is seen superimposed on the large scale fluctuations. It indicates the existence of smallgrains, and is proof of the nanocrystalline structure of the films. Although the exact value of the grain size cannot be obtained, a rough estimation based on Figs.1 (a) and (b) gives values less than 10 nm.

The standard CPM gives the absorption coefficient α in arbitrary units. As is usually done, in order to obtain α in absolute units (cm^{-1}), we used data from standard optical measurements published in [12]. The relation $\alpha \sim (E - E_g^o)^{1/2}$ (E - energy, E_g^o - optical band gap) typical for crystalline semiconductors with a direct optical band gap was applied to determine E_g^o for the $AgBiS_2$ films investigated. Figs. 2 (a) and (b) show the αE^2 vs. E dependences obtained for two films. They display good linearity, thus confirming that the grains in the layers are of a good crystalline structure. A value of 1.11 eV was determined for the E_g^o of one film (Fig. 2 (a)), which is in excellent agreement with the value obtained from the optical measurements (1.10 eV [12]). It is higher than the E_g^o value of bulk $AgBiS_2$ (0.9 eV), and indicates that carrier confinement takes place in each grain of the nanocrystalline layers. It causes changes in the electronic structure of the $AgBiS_2$ nanocrystalline layers, in particular an increase in the optical band gap.

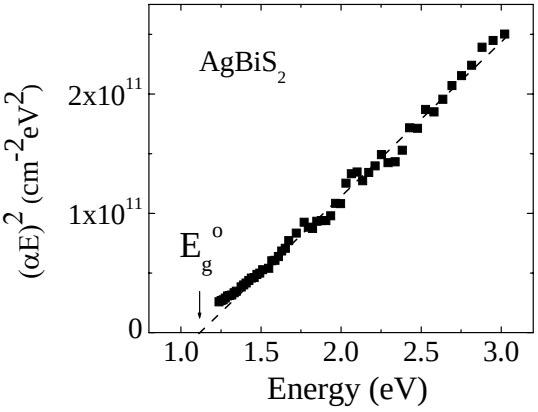

Fig. 2. Typical αE^2 vs. E dependence obtained for an $AgBiS_2$ film. The data point spreading is due to the fine structure discussed in the text.

Normalized absorption spectra of three $AgBiS_2$ thin films with different thicknesses are shown in Fig. 3. Several maxima are resolved, situated at the same energies in all samples (~ 1.5, 1.75, 2.05 and 2.25 eV). No interference has been observed in the optical transmission spectra of all layers (the layer thickness was < 200 nm). This indicates that the features observed are not due to light interference but are inherent characteristics of

nanocrystalline $AgBiS_2$. Most likely, the observed fine structure represents electronic transitions related to higher excitons. Its appearance implies a narrow size distribution and a good spherical shape of the nanocrystal grains.

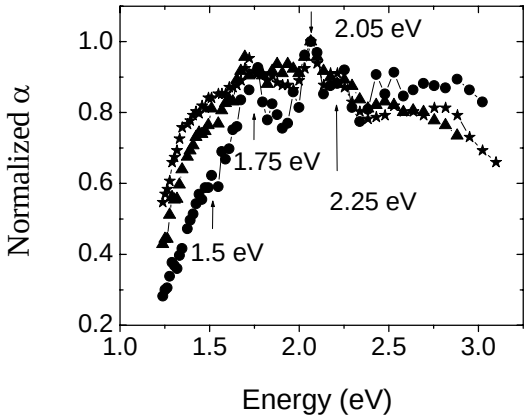

Fig. 3. Normalized absorption coefficient α versus energy of three $AgBiS_2$ thin films. The spectra were obtained by CPM measurements.

Fig. 4 depicts the temperature dependences of the photocurrent measured on an $AgBiS_2$ sample at two different intensities. The measurements were carried out: (i) after preliminary heating in the dark without an applied voltage or (ii) after preliminary light exposure under an applied voltage. One can see that in the former conditions, the sample shows a flat and low photoconductivity in the low-temperature range, and a gradual increase at $T > 250^oK$. Such a temperature dependence is typical for disordered materials [14] which contain a high density of fast recombination centers. Normally, good crystalline photoconductors display a high photoconductivity at low temperatures, and often display thermal quenching [15]. Such behaviour is explained with a relatively low bulk concentration of fast recombination centers. The results in Fig. 4 indicate that the recombination of photoexcited carriers is mainly via fast recombination centers, whose density should be quite high. Keeping in mind the above conclusion that the grains are crystalline rather than amorphous, one can assume that interface defects play the role of fast recombination centers. This suggestion can explain the low photoconductivity measured [12] on sonochemically prepared $AgBiS_2$ films, in which the grain size is considerably smaller than that in chemically produced ones.

The spectra measured without preliminary annealing show (Fig. 4) a significantly higher photoconductivity at low temperatures, which is practically independent of the light intensity. After turning off the light a very similar dark current is observed, and it decreases very slowly with time. This phenomenon is known as residual (or persistent) photoconductivity. It has been observed in various thin films, and it is related to carrier trapping in deep defect states or to charge separation at the interfaces between the grains. Normally, the photocurrent in such films displays a weak intensity dependence in the temperature range of the existence of persistent photoconductivity; the lower the temperature, the higher the sub-linearity of the dependence.

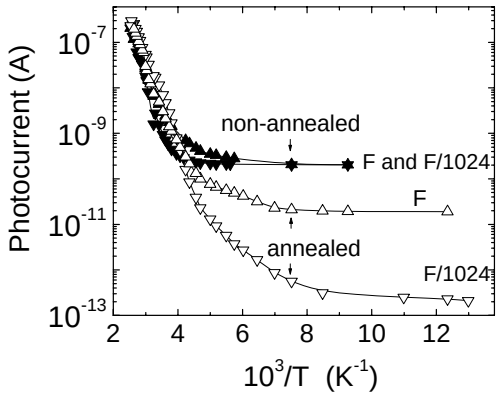

Fig. 4. Temperature dependences of the photocurrent of an $AgBiS_2$ film measured under illumination with two light intensities as shown. The open symbols correspond to the preliminary annealing of the film at 120^oC, while the filled symbols represent curves measured without annealing.

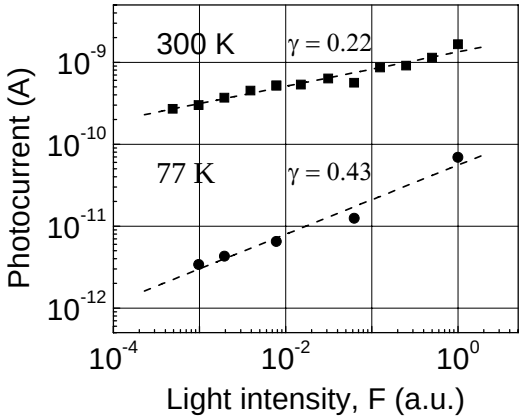

Fig. 5. Intensity dependence of the photocurrent, $I_{ph} \sim F^{\gamma}$. The value of the exponent γ indicates strong sublinearity.

Fig. 5 shows a pronounced sub-linearity at both 77 and 300 K, but it is more strongly pronounced at 300 K. In order to clarify the reason for this result, we studied the so called high field polarization observed in highly resistive materials. It is due to trapping of non-equilibrium carriers near the contacts or in the sample bulk, and results in the creation of an internal electric field with an opposite polarity to the external one. This causes a decrease in both the dark- and photo-currents. A photocurrent decrease has been observed for the studied $AgBiS_2$ films upon applying

electric field and light exposure at the same time. The smaller value of the exponent γ at 300 K could be due to the observed stronger polarization at this temperature.

4. Conclusions

Chemically produced nanostructured $AgBiS_2$ thin films have been investigated. AFM measurements have shown that the films are nanocrystalline, with a grain size smaller than 10 nm. Fine structure has been observed in the absorption spectra, which implies a narrow size distribution and a good spherical shape of the nanocrystals. Based on the temperature dependences of the photocurrent measured in the range 77 – 390 K, it has been assumed that fast recombination centers, dispersed at the intergrain interfaces cause a reduction in the photoconductivity, in particular at low temperatures. The observed rather low exponent in the photocurrent intensity dependence has been connected with persistent photoconductivity.

Acknowledgements

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