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OPTICAL CHARACTERIZATION OF NANOSTRUCTURED $CUINS_2$ BY SPECTROSCOPIC ELLIPSOMETRY

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The powdered samples of $CuInS_2$ obtained by a chemical synthesis method and contained either thread-like or belt-like nanowires were studied by a spectroscopic phase-modulated ellipsometer in the photon energy range 0.8eV to 6eV at room temperature. The samples with thread-like and belt-like nanowires were found to have different pseudodielectric function, which was closer to that of bulky single crystalline $CuInS_2$ in the case of belt-like nanowires. The same value of energy gap revealed by incoherent ellipsometric approach to bulky samples and samples with nanowires was accounted for the presence of some fraction of bulky phase in the nanostructured samples.

Reliability of the obtained data and relationship between the ground state shape of the nanowires and the electronic spectrum were discussed. It was substantiated that the obtained data provide a first realistic glimpse on electronic spectrum of nanostructured $CuInS_2$.

1. INTRODUCTION

Single crystals and thin films of $CuInS_2$ (CIS) have been studied worldwide in relation with high-efficient solar cells based on this material [1,2]. Recently Y. Jiang *et al* [3] have reported the first preparation of CIS-nanowires by a chemical treatment method, which provides a path to the nanostructured CIS.

Along with big interest to all materials with nanostructures, the studies of the nanostructured CIS may yet be important for the simplicity and low cost of the preparation method [3,4], since nanostructured CIS may turn to be a low cost substitute for CIS single crystals and thin films, which require quite complex technology for preparation and are rather expensive [5-7].

Perhaps the key element making CIS so advantageous by comparison with other photovoltaic materials is the optimum band gap to solar irradiation [8] and the electronic spectrum of the nanostructured CIS as compared to bulky or thin film form of this material is definitely among the key issues to be addressed in the first place.

Room temperature electronic spectrum of CIS single crystals has already been studied by spectroscopic ellipsometry and the obtained results have been found to fit well into the conventional band structure used for all Cu-based compounds with tetragonal chalcopyrite structure [9].

In this work we also use spetroellipsometric experimental approach in trial to provide a first glimpse on electronic spectrum of nanostructured CIS.

2. EXPERIMENTAL DETAILS

2.1 Samples

CIS nanowires were synthesized using a chemical treatment method similar to the reported by Jiang *et al* [3]. Pure copper, indium, and sulfur powders were placed in a stainless steer reactor filled with ethylendiamine as solvent. After sealing, the reactor was put in an electric furnace and kept for 24 hours at a temperature between 280 and 300^{o}C.

The obtained product was then extracted, washed in water and alcohol, and annealed in vacuum for 6 hours at 60^{o}C.

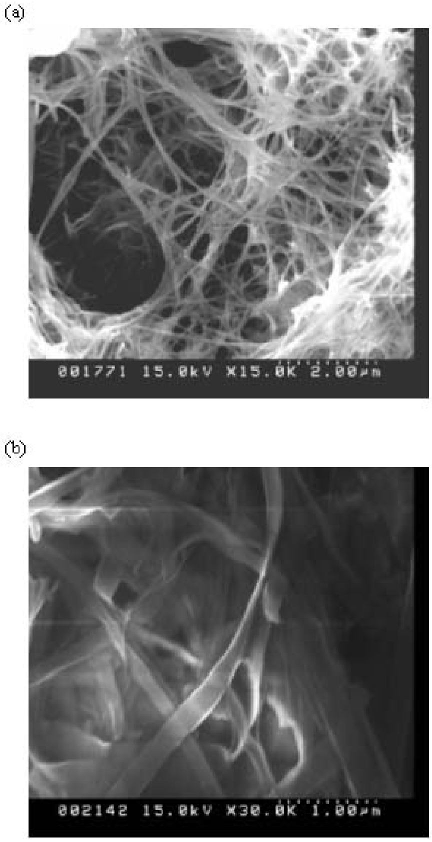

Fig.1 CIS samples with thread-like (a) and belt-like (b) nanowires

X-ray diffraction patterns of the final products were examined using CuK$_{\alpha}$ radiation, and found to be close to the bulky chalcopyrite structure of CIS with lattice parameters a=b=5.523 Å and c= 11.141 Å.

To an extent given by FE-SEM (field emission - scanning electron microscopy) examination, in all cases the final products were populated with either thread-like (Fig. 1a) or belt –like (Fig. 1b) nanowires depending upon conditions of synthesis.

The thread-like nanowires were 30-100nm in diameter and several micrometers in length. The belt-like nanowires were represented by wide (up to several micrometers) lengthy (several micrometers) strips with thickness of 30-50nm.

The samples for ellipsometric measurements were prepared by pressuring the above nanowired product into the tablets with a diameter of 5mm. The tablets were then examined by a high-grade optical microscope to get a view of the surfaces to be probed by a 0.5mm diameter light beam of a Jobin-Yvon spectroscopic phase-modulated ellipsometer (SPME). The surfaces of the tablets with nanowires, whether thread-like (Fig. 2a) or belt-like (Fig.2b), turned out to be rough and the ellipsometrically obtained pseudodielectric function given later in this paper should be regarded with some reservations for the effect of the surface roughness.

2.2 Ellipsometric approach

The problem of the restoration of the dielectric function from ellipsometric measurements on roughened surfaces has not been settled yet. In our present ellipsometric studies we have tried to follow the experimental approach [10,11] because the observations made in the works [10, 11] provide a clue to the performance and data-treatment for ellipsometric measurements on random, strongly scattering media with arbitrary parameters.

3. RESULTS

3.1 Polarization degree

For non-depolarizing samples the ellipsometric angles Ψ and Δ are known to be the unique parameters unambiguously related with the dielectric function. However, in case of roughened surfaces, above angles are influenced by depolarization that might be so strong that it can even lead to a partial or total loss of the coherency of the light reflected by the sample [10].

In Fig. 3 we have shown the polarization degree (P) of the light reflected by our samples in a wide range of photon energies. The shown behavior is typical for all samples, whether with thread like or belt-like nanowires, and indicative of the loss of the light coherency at the energies below 1.51eV. Such a situation is not much of surprise because the last energy is exactly the excitonic band gap of bulky CIS and the depolarization effects (if any) are supposed to be stronger exactly in the regions below the energy gap.

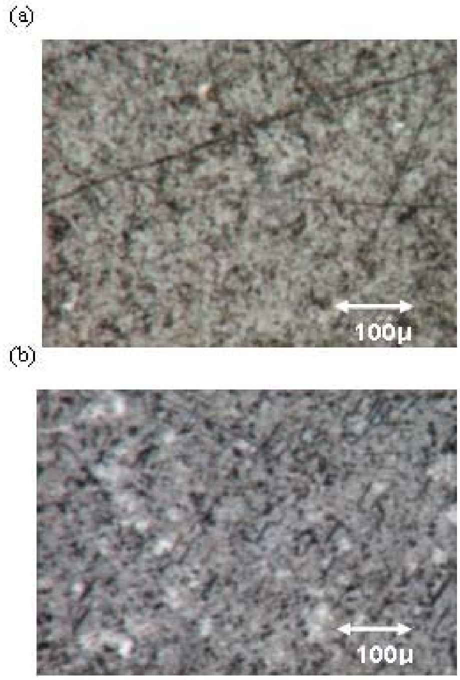

Fig.2 Surface fragments of CIS tablets with thread-like (a) and belt-like (b) nanowires.

A remarkable drop of P (Fig. 3) just around the band gap singularity is similar to that observed ellipsometrically earlier by M. Kildemo *et al* [12] in relation with the incoherent reflection from thick glass substrates. The only difference is that in our case incoherent scattering rather than incoherent reflection has stepped into play.

Since incoherent scattering is caused by sample roughness, the later is taken into account automatically. Therefore above results can be regarded as quite rigorous with regard to the value of the energy gap of our nanowired samples.

"The goodness" of the standard pseudo-dielectric excitons in bulky CIS is shown by vertical arrow.function in application to the roughened surfaces depends upon the characteristic scale of the elements (grains) from which the sample is composed. And the larger this scale is in comparison with the utilized light wavelength the better the pseudo-electric function is representing the dielectric function of the material [10, 13].

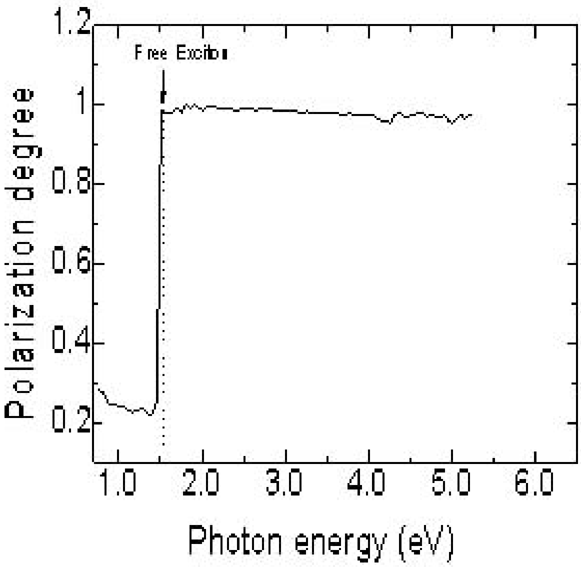

Fig.3 Photon energy dependence of polarization degree of the light specularly reflected by nanowired samples into an angle of 60^{o}. Energy position of free

In our case extended measurements of P have shown that P is irregular with incident angle. According to the results of the work [10] such behavior of P is a sign of the large grain sizes as compared to light wavelength. Note that such a conclusion is, in no way, inconsistent with the small lateral dimensions of the obtained nanowires and only points to the fact that the investigated samples were macroscopically rough.

3.2 Pseudodielectric function

The pseudodielectric function (PD) restored from the spectroellipsometric data at incident angles for which P was close to 1 in the whole range of the photon energies accessed during experiments is shown in Fig. 4. Single crystalline CIS that we investigated as a reference system with smooth surface for comparison is also included in Fig. 4 (curves 1).

One can notice that in both real (Fig. 4a, curve 2) and imaginary (Fig. 4b, curve 2) parts of PD of the samples populated with belt-like nanowires are enough of resemblance with bulky CIS (curves 1 in Fig. 4a and 4b, respectively), up to the band gap excitonic singularity in the position of its appearance in bulky samples. At the same time, a new structure is evident in the region above the energy gap, as indicated by a vertical arrow in Fig. 4.

Apparently, the changes in both the real (Fig. 4a, curve 3) and imaginary (Fig. 4b, curve 3) part of PD look more dramatic for the samples with thread-like nanowires and one might even have an impression that the band gap of these samples is larger than usual. But, this is not true, of course, since the correct value of the band gap energy of a sample as a whole is provided by incoherent ellipsometric approach rather than restored pseudodielectric function.

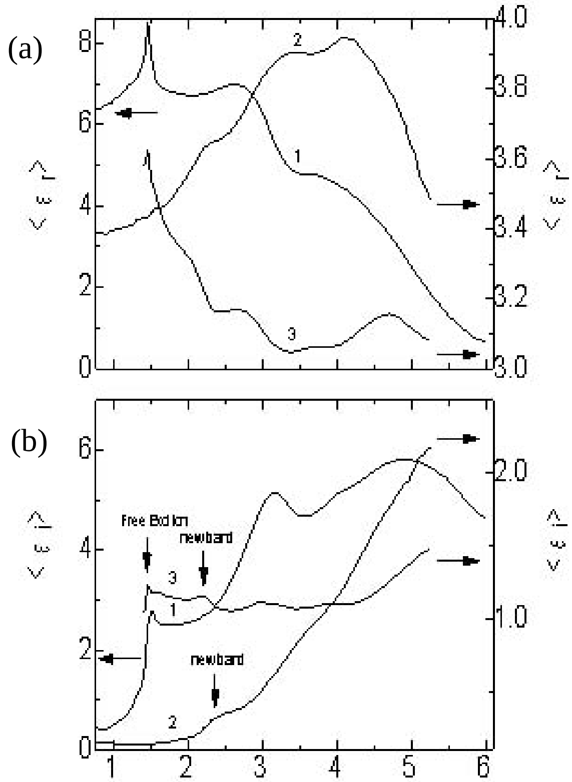

Fig. 4 Real ((a)-$\langle \varepsilon_r \rangle$) and imaginary ((b)-$\langle \varepsilon_i \rangle$) parts of pseudodielectric function of single crystalline CIS (curves 1), CIS with belt-like nanowires (curves 2), and CIS with thread-like nanowires (curves 3). New bands as compared to bulky CIS are shown by vertical arrows.

At the same time one must remember that if a sample contains some admixture of an alien phase having small energy gap by comparison with main phase, the incoherent ellipsometry will display the band gap of this alien phase even if a fraction of this phase is negligible. On the other hand, coherent ellipsometric approach using which PD was restored is less sensitive to the amount of the alien phase and we believe that the observed differences between the samples with belt-like and thread-like nanowires enough realistically represent the changes occurring in PD of nanostructured samples. In quantitative accounts the effect of the roughened surface is, of course, unavoidable but qualitative features of PD are believed to be displayed by Fig.4 (curves 2 and 3). Also note that high-grade optical microscope images of the nanostructured samples reveal no difference in the roughness between the samples with belt-like (Fig. 2a) and thread-like (Fig.2b) nanowires. At the same time PD of the samples has noticeably changed.

4. DISCUSSION

We are not in an opinion that the changes in PD described above have resulted from the quantum size effect in the nanowired samples because the nanowires were “thick”, (Section 2.1). At the same time, some changes in PD are certainly favorable since the ground state shape of the nanowires has in fact been changing from belt-like to thread-like. But, the ground state shape is the derivative of the balance between the surface and bulk energies in the minimized Wulff energy construction [14] and the change of the ground state shape should inescapably lead to the modification of the electronic spectrum, as a whole.

We are in opinion that, in spite of the roughened surface of the investigated samples, their PDs (Figs 4a and 4b, curves 2 and 3) are indicative of such changes at least on a qualitative basis. The same energy gap that was displayed by incoherent ellipsometry for bulky and nanowired samples is very likely to be a result of the presence of some fraction of bulky phase in the samples populated with nanowires. Such a conclusion is quite consistent with the results of our recent photoluminescence (PL) studies [4] performed before and after the samples with nanowires were pressurized into tablets. According to the obtained results [4] the maximum of PL near band edge was noticeably shifted toward higher energies when we passed from the bulky sample or sample with belt-like nanowires to the sample with thread-like nanowires.

5. CONCLUSIONS

We have carried out the ellipsometric studies on the nanostructured CIS and have shown that the gap energy of bulky CIS and the samples with nanowires is practically the same. However, the constancy of this energy is probably because of the presence of some fraction of bulky phase in samples with nanowires. The electronic spectrum, as a whole, undergoes certain changes displayed by comparison of PD of bulky CIS with that of the samples with belt-like and thread-like nanowires.

Although this work is not entirely comprehensive and further studies are necessary to better understand the nature of the structures observed in the pseudodielectric function of samples with nanowires, we believe that the obtained data provide a first realistic glimpse on electronic spectrum of the nanostructured CIS.

ACKNOWLEDGMENTS

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