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ИССЛЕДОВАНИЕ КОМБИНАЦИОННОГО РАССЕЯНИЯ МАТЕРИАЛОВ НА ОСНОВЕ CdS

Показано, что спектроскопия комбинационного рассеяния света является действенным методом исследования материалов на основе аморфного CdS. При этом выбор длины волны возбуждения имеет определяющее значение. Использование излучения с длиной волны 1064 нм оказалось более предпочтительным, чем с 514,5 нм. Фундаментальные особенности эффекта комбинационного рассеяния позволяют установить существование полимерной структуры CdS. Было обнаружено, что различные материалы на основе поливинилового спирта (ПВС) имеют сходные спектры комбинационного рассеяния. Из этого делается вывод, что такие материалы обладают сходными свойствами и структурой интерполимерных комплексов, аналогичной двойной спирали ДНК. Одним из компонентов такого комплекса является ПВС, а другим – неорганический полимер. Введение примесей позволяет кардинально изменить свойства материала, определяющие вид спектра комбинационного рассеяния и выявить в нём неактивные молекулярные колебания. Установленный подход можно применять как стандартный метод исследования подобных материалов.

Ключевые слова: гибридные интерполимерные комплексы, поливиниловый спирт, структура CdS, неорганические полимеры, одномерные структуры, комплекс поливиниловый спирт-йод.

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RAMAN SPECTROSCOPY INVESTIGATION OF CdS BASED MATERIALS

It is shown that Raman scattering is useful tool of amorphous CdS based materials investigation. Excitation wavelength has crucial importance in this case. 1064 nm excitation turned out more preferable then 514.5 nm one. New polymeric structure of CdS is determined by Raman scattering due to its fundamental principles. It was discovered that different materials based on polyvinyl alcohol (PVA) have similar

Raman spectra. The conclusion was made that these materials have similar properties and structure of interpolymeric complexes like double DNA helix. One component of such complex is PVA and another one is inorganic polymer. Impurity doping allows to change drastically Raman behavior and reveal hidden molecular oscillations in these systems. Elaborated approach can be used as a template for the investigation of similar materials.

Keywords: hybrid interpolymeric complexes, polyvinyl alcohol, CdS structure, inorganic polymers, one-dimensional structures, polyvinyl alcohol-iodine complex.

Introduction

One-dimensional structures attract significant attention due to their expected valuable properties which follow from quantum-size effects. Ballistic conductivity is an example of such behavior [1]. Unfortunately, there is a lack of true one-dimensional systems like polymers suitable for some applications. For example, it is not easy to produce highly conductive or luminescent polymers. The number of known inorganic polymers is not high and it is desirable to increase it. One way of inorganic polymers production was suggested earlier [2]. It is based on a synthesis of hybrid interpolymeric complexes of complexing organic polymers like polyvinyl alcohol (PVA). The well-known representative of such compounds is PVA-iodine complex [3]. It was suggested that hybrid interpolymeric PVA-CdS complex can also be synthesized [4, 5]. The problem is a confirmation of polymeric structure due to absence of three-dimensional periodicity. Raman and IR spectroscopy can help in this case. Oscillation frequencies of inorganic structures usually are out of common IR spectrometers’ range. Therefore, Raman spectroscopy gains high importance. On the other hand, Raman scattering is stipulated by influence of molecular oscillations on molecular polarizability. It means that Raman spectrum features are determined by electrical properties of investigated material and we can use it not only for structure determination but also for other research purposes. In this paper we describe such implementation of Raman spectroscopy to PVA-CdS compound’s structure investigation in more details then in previous brief report [5].

Experimental

PVA-CdS samples preparation was described earlier [5]. PVA is widely used for nanostructured CdS preparation [6-11], but synthesis always went through liquid medium. In our case synthesis went in solid state. We believe that it allows to produce and stabilize polymeric CdS structure inherited from polymeric $CdCl_2$ structure of PVA-$CdCl_2$ complex [12]. Monocrystalline CdS with hexagonal structure was presented by a Laboratory of Nonlinear Resonant Processes and Laser Diagnostics of Institute of Semiconductors

Physics, Novosibirsk, Russia. Reference PVA-iodine complex was prepared by keeping of PVA film in ortho-xylol I_2 solution.

Raman measurements were carried out with Bruker RFS-100/S spectrometer equipped by 1064 nm excitation source and with Horiba Jobin-Yvon T64000 spectrometer equipped with 514.5 nm laser. All spectra were measured at room temperature; registration conditions were chosen in such a way as not to cause local heating of the films by laser radiation.

Results and discussion

Raman spectra of monocrystalline (wurzite) CdS sample obtained at different excitation wavelengths are presented in fig. 1 and fig. 2. Raman band at 305 cm^{-1} and its two-phonon repetition at 610 cm^{-1} were earlier reported in crystalline CdS spectra at Ar laser 488 nm excitation [13]. Our result exhibits broad band at 300-380 cm^{-1} at 514.5 nm excitation. It is in general accordance with other researches carried out with excitation wavelength not exceeding 532 nm [6-9, 13-21]. There are few reports with 1064 nm excitation of CdS nanoparticles and films [10, 11] where bands at 556(558), 785(799) and 1094(1096) cm^{-1} were observed but not 300 and 600 cm^{-1} bands. Our measurements at 1064 nm excitation show distinct lines at 212, 235, 252, 325, 345, 560, 595 cm^{-1} and several unresolved lines for monocrystalline (hexagonal structure) samples. But quality of spectra drops sufficiently after crystal grinding. This result is in accordance with earlier observations at 632.8 nm off-resonance excitation [22]. One can be concluded that Raman band at 305 cm^{-1} (and its repetition at 610 cm^{-1}) dominates in spectra of CdS based materials at excitation wavelength not exceeding 532 nm. At longer wavelength excitation intensity of this band decreases and other bands become more intensive. Such unexpected behavior of CdS Raman scattering is known and has explanation [23].

The second interesting peculiarity of PVA-CdS compound Raman behavior is similarity with other PVA based compounds’ spectra. Such similarity of PVA-CdS and dehydrated PVA Raman spectra has been reported earlier [5] and attributed to SERS-like (Surface Enhanced Raman Scattering) effect. Dehydrated PVA is a kind of polyacetylene [24]. It is turned out that mentioned above Raman spectra also are similar to PVA-iodine complex’ spectrum (fig. 3). They were recorded at 1064 nm excitation. In these spectra we can see two distinguished broad bands at 1110 and 1480 cm^{-1} and prominent background. The band at 2900 cm^{-1} is manifestation of the most intensive band of pure PVA. After extraction of iodine from the sample its Raman spectrum became similar to pristine PVA Raman spectrum. Measurements at 514.5 nm excitation give another picture for PVA-CdS sample. The 300 cm^{-1} band and intensive background associated with fluorescence are presented in it (fig. 4). To suppress the elastically scattered light (Rayleigh scattering of 514.5 nm laser line), an edge filter is installed before front of the entrance slit of the T64000 monochromator. The transmission characteristics of this filter for light with a wavelength greater than 514.5 nm are not monotonic due to interference effects in the filter. Therefore, against the background of a wide fluorescence band, "artifacts" associated with interference in the filter are visible simultaneously with quite narrow and intense 300 cm^{-1} Raman peak.

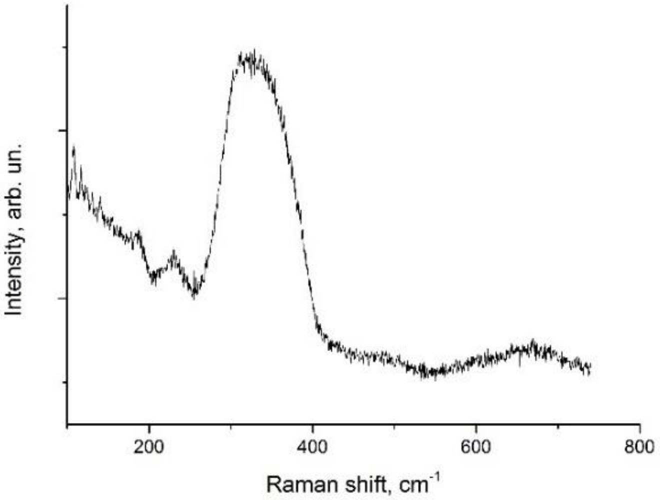

Fig. 1. Raman spectra of monocrystalline (wurzite) CdS. 514.5 nm excitation

For PVA-iodine samples measurements at 514.5 nm excitation give picture the similar to spectrum at 1064 nm excitation (fig. 5). Background, two shifted strong bands at 1130 and 1515 cm^{-1} and weak band at 1295 cm^{-1} are observed. Well-known PVA-iodine complex has been thoroughly investigated [3, 25-27]. It was determined that it consists of linear $-(I_3)_n-$ or $-(I_5)_n-$ polymeric chains complexed with PVA chains like components of DNA (deoxyribonucleic acid) double helix. Similarity of Raman spectra indicates similarity of structures and properties. Therefore, we can conclude that CdS synthesized in solid PVA matrix has a structure of $-(CdS)_n-$ conjugated polymer in contrast to other CdS based materials. Fortunately, this system is transparent for visible light in opposite to polyacetylene and PVA-iodine complex what gives hope for polymeric transparent conductive films creation.

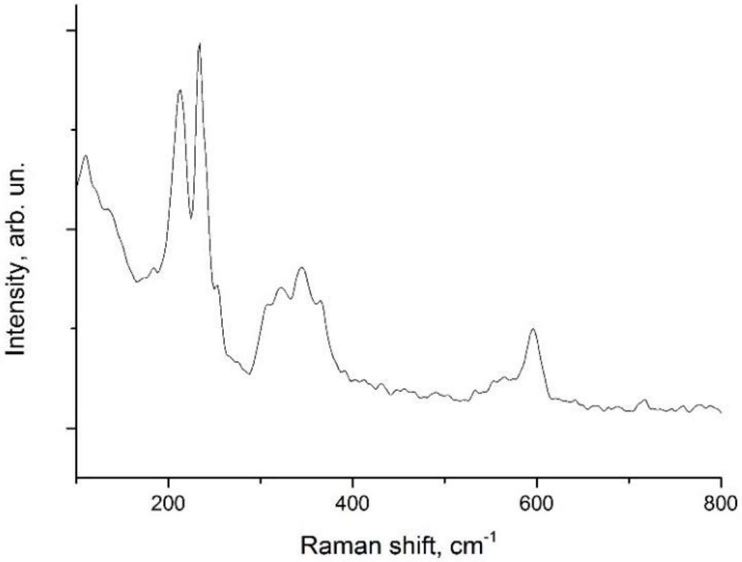

Fig. 2. Raman spectra of monocrystalline (wurzite) CdS. 1064 nm excitation

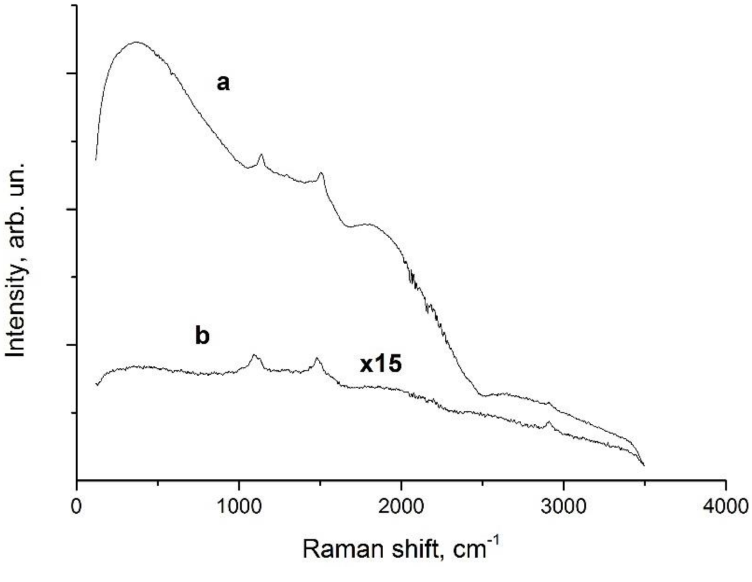

Fig. 3. Raman spectra of PVA-CdS compound (a) and PVA-iodine complex (b).
1064 nm excitation

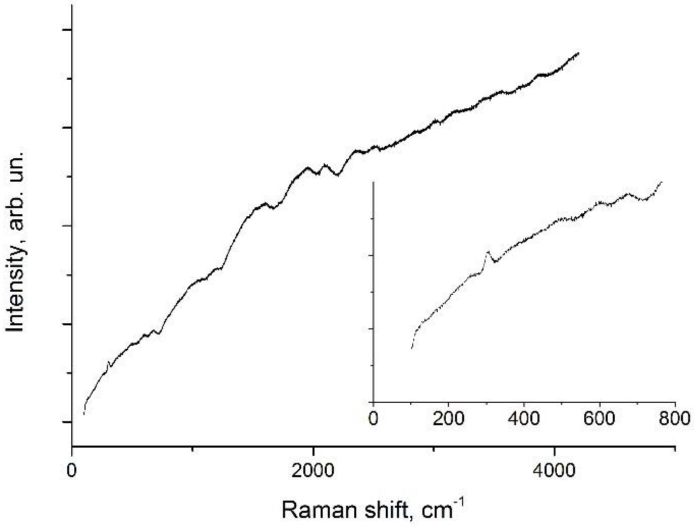

Fig. 4. Raman spectrum of PVA-CdS compound. 514.5 nm excitation

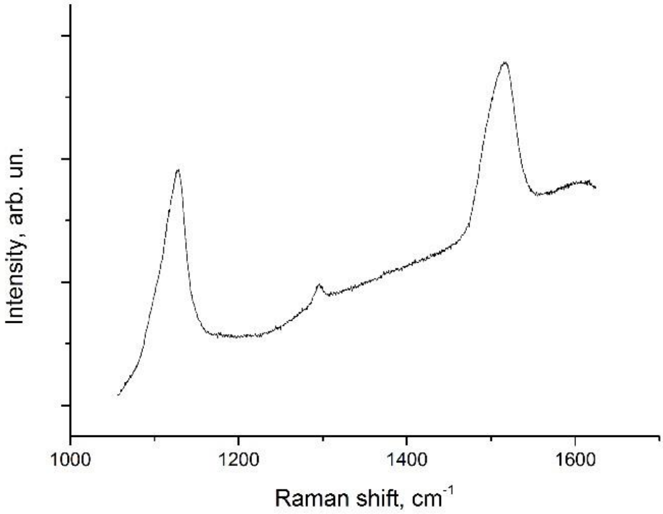

Fig. 5. Raman spectrum of PVA- iodine complex. 514.5 nm excitation

The next peculuarity of PVA-CdS compound Raman behavior is its high sensitivity to impurities. It was reported that doping by ~1 wt. % (to CdS) Al and Mn leads to drastic Raman spectrum change – background decrease and PVA bands appearance [5]. In addition to PVA bands one new band at 230 cm^{-1} appears (fig.6). This band we attributed to oscillation of polymeric CdS. This effect was explained by change of polarizability of CdS chains. Doping with Al leads to polymeric chain termination: S=Al-S-Cd- and to conjugation length and polarizability decrease. Doping with Mn leads to resistivity of polymeric chains to molecular current increase and hence polarizability decrease. We suppose that polarizability of described systems is determined by (macro)molecular currents. High anisotropic polarizability depends weakly from molecular oscillations along the polymeric chain and these oscillations don't manifest they self in Raman spectra. Transversal oscillations can make higher influence on polarization and hence they can give strong bands in Raman spectrum. Low polarizability depends stronger from atomic displacements and all oscillation bands appear in spectrum. Raman band at 230 cm^{-1} was also reported for CdS film modified by Cu^{+} implantation [15] at 488 nm excitation. Its attribution to different oscillation modes was discussed. Our measurements at 514.5 nm excitation did not show drastic change of Raman spectra of doped samples (fig. 7) that can be explained mentioned above peculiarity of CdS Raman scattering.

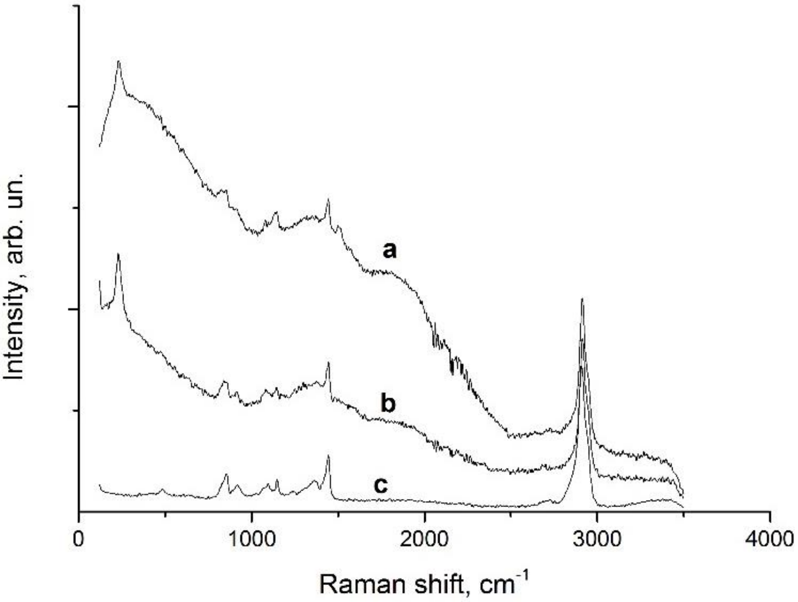

Fig. 6. Raman spectra of PVA-CdS compound doped with Al (1 wt. % of CdS) (a), doped with Mn (2 wt. % of CdS) and pristine PVA (c). 1064 nm excitation

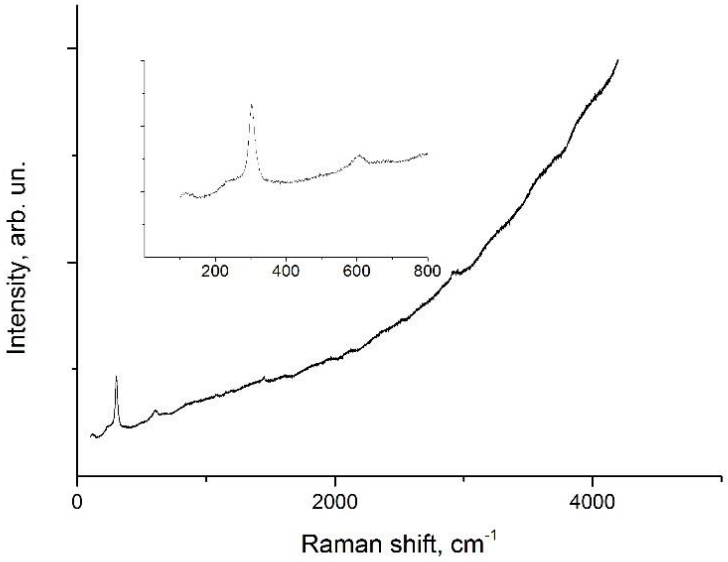

Fig. 7. Raman spectra of PVA-CdS compound doped with Al (1 wt. % of CdS).
514.5 nm excitation

Conclusion

Some observed peculiarities of PVA-CdS compound Raman behavior can be explained by conjugated polymeric CdS structure formation. Described procedure based on Raman measurements is suggested for identification of new inorganic polymeric structures.

High sensitivity of CdS based materials' Raman spectra to excitation wavelength should be taken into consideration at excitation wavelength selection.

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