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Materials Science in Semiconductor Processing 8 (2005) 576–586
MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING

Band gap in tungsten sulphoselenide single crystals determined by the optical absorption method

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Received 7 March 2005; received in revised form 19 July 2005; accepted 28 July 2005
Available online 10 October 2005

Abstract

Optical absorption in single crystals of tungsten sulphoselenides has been measured at room temperature with the incident light beam normal to the basal plane, i.e. along *c*-axis of the grown crystal flakes. Results have been analysed on basis of two-dimensional (2D) and three-dimensional models (3D). Absorption near the fundamental edge was found to be due to indirect allowed transition on the basis of (3D) model and due to indirect forbidden transition on the basis of a (2D) model. Both transitions involve two phonons. The energy gaps and phonon energies have been estimated. The indirect and direct band gaps of WS_xSe_{2-x} vary smoothly with the S/Se composition x, indicating that the nature of band edges is similar for WSe_2, WS_2 and compounds of intermediate composition. The dependence of band gaps on sulphur/selenium content in WS_xSe_{2-x} has been adequately explained on the basis of band structure calculations reported in the literature.

PACS: 81.10B

Keywords: Vapour transport; Absorption spectra; Band gap; Transition metal–dichalcogenides; Semiconductor

1. Introduction

The band gaps of many transition metal–dichalcogenides (TMDCs) are around 1 eV and it has been suggested that the band gaps are indirect. Evidence for this is provided by the band structure calculations carried out so far. Sharma et al. [1] give comparison of the valence band maximum (VBM), conduction band minimum (CBM) and band gaps E_{gap} for WSe_2 obtained by different band structure calculations and experiments. It is quite clear from this work that regarding the indirect transitions two quite distinct schemes are proposed.

In the first scheme [2] the VBM is at the zone centre Γ and the CBM is on the Γ line half-way between Γ and K. Experiments supporting this scheme give the value of indirect band gap as 1.20 eV.

In the second scheme [3], the VBM is situated at the six-fold degenerate K-point of the Brillouin zone. The indirect transitions across the gap occur between the K-point and the conduction band minimum at 0.5 ΓK. The experiments in support of this scheme give the value of indirect band gap as 1.30 eV. Regarding direct transitions

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doi:10.1016/j.mssp.2005.07.001

also there are two distinct schemes, which are still proposed.

In the first model [4], the direct gap could be due to the d→d type transitions at Γ from the filled d_z^2 orbital to a pair of $d_{x^2-y^2}$, d_{xy} states.

In the second quite recent model [5], the direct gap is due to transitions at the K-point of the Brillouin zone.

In order to gather experimental evidence for the indirect and direct nature of the gap in some of the TMDCs we find that photoemission data [6] and first principles band structure calculations [7] for MoS_2 (a structure to which WS_2 and WSe_2 belong) predict a band gap which is less than the energy of the A exciton but greater than 0.3 eV. They predict an indirect gap of ~1.1–1.2 eV and a direct gap of 1.6 eV. Therefore, in an attempt to determine the nature and magnitude of the energy gap in MoS_2 and in compounds possessing MoS_2-type structure, one should concentrate on absorption measurements below the A exciton energies. In fact, Parenteau and Carlone [8] have shown that it is possible to obtain both direct and indirect band gaps simultaneously from the plot of absorption coefficient α versus $h\nu$. Goldberg et al. [9] did study the low absorption edge in 2H-MoS_2 and 2H-$MoSe_2$. They fit the absorption edge to that expected for direct and indirect transitions finding a better fit for the indirect process. There is good experimental evidence that the edge is indirect in MoS_2, $MoSe_2$ and WSe_2 from the spectral dependence of the photoyield of electrochemical cells [10], but the involvement of phonons has only been shown by Kam et al. [11]. There is therefore enough scope for a detailed analysis of the absorption spectrum in the region of indirect transitions for studying the involvement of phonons in the indirect transition. At the same time, an analysis of the absorption spectrum in the region of direct transition below the A exciton will provide the value of the direct gaps in TMDCs.

In order to increase the range of applicability of binary MX_2 TMDC compounds in device fabrication, partial cation substitution has proved to be a useful tool for manipulation of optical band gap [11]. There has also been an effort to exploit anion replacement as a way to fine-tune the optical band gaps by Ortiz et al. [12]. But these authors have worked on mixed polycrystals of WS_xSe_{2-x} and moreover they have not been able to show the involvement of phonons in the indirect transitions. Joshi et al. [13] studied the electrical properties of WSSe single crystals grown by both direct vapour transport (DVT) and chemical vapour transport (CVT) methods. They found that crystals grown by DVT were less resistive and p-type semiconducting in nature while those obtained by CVT were highly resistive, n-type and more stoichiometric. This gave rise to observed differences in their electrical characteristics. Further, Vashi et al. [14] carried out convergent beam electron diffraction (CBED) studies on WS_xSe_{2-x} ($0 \leqslant x \leqslant 2$) single crystals grown by a DVT technique. They found all crystals of WS_xSe_{2-x} to be mixed polytypes of 2H and 3R except WSe_2 which exhibited only 2H polytypic behaviour. CBED patterns taken at different temperatures indicated no phase transformation, only an increase in the value of 'c' with increase in temperature was noted. Recently Patel et al. [15] studied the effect of partial replacement of selenium by sulphur in the lattice of WSe_2 on the photoconvesion behaviour of WSe_2 PEC solar cells. They observed that such a replacement of selenium by sulphur does not yield any improvement in the PEC behaviour of WSe_2. However, none of these studies [13–15] refer to the effect of compositional variation of S/Se in WS_xSe_{2-x} on the optical band gap. In the following therefore, authors report on the measurement of absorption edge of single crystals of WSe_2 and of several mixed crystals of WS_xSe_{2-x} where a partial and total replacement of selenium has been made by sulphur. A thorough analysis of the data obtained during the course of the experiments has been described in this paper.

2. Experimental

The main aim of the work presented in this paper is to study optical band gaps in WS_xSe_{2-x} and to see the effect of replacement of selenium by sulphur in WSe_2 first of all partly and then totally on the optical band gap of this material. Accordingly all samples of WSe_2, $WS_{0.5}Se_{1.5}$, WSSe, $WS_{1.5}Se_{0.5}$ and WS_2 used in the present work were grown by the chemical vapour transport technique [16]. Large single crystals having black opaque appearance with perfectly shining surfaces were obtained. Their single crystallinity and compositions were verified through transmission electron diffraction and energy-dispersive analysis of X-rays (EDAX), respectively. All the crystals had proportionate elemental composition and were nearly stoichiometric. EDAX analysis did not reveal the presence of any secondary phases in them. Since the crystals grew