Temperature dependence of the optical absorption edge of pyrite FeS$_2$ thin films

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Abstract. Optical absorption edge measurements of pyrite thin films prepared by flash evaporation have been made at different temperatures in the range 10–300 K. Absorption edge values vary from 1.05 to 0.99 eV in that temperature interval. Experimental data have been fitted to the Varshni formula and to an expression proportional to the statistical Bose–Einstein factor used previously by other workers. The main phonon energy calculated from the fitting of the experimental points to the Bose–Einstein expression is in good agreement with the average energy of the active optical phonons as determined by Raman spectroscopy carried out on the same pyrite thin film.

1. Introduction

Knowledge of the temperature influence on the optical absorption edge E_0 of semiconductors is of interest in order to check band-structure calculations and to define their future and new applications. Pyrite is receiving growing attention because of its promising potential for use as an optoelectronic and/or photovoltaic material [1–3]. Both single crystals and polycrystalline thin films are extensively investigated nowadays. However, it is difficult to establish a final statement on its real possibilities owing to the uncertainty in the available information on E_0 and its temperature dependence. Values of the pyrite absorption edge at RT have been determined by many workers and it has been found that it strongly depends on the nature of the material (single crystals, thin films, etc.) and on the experimental method used to measure it. This matter has been recently reviewed [4]. On the other hand, the influence of temperature on the pyrite absorption edge has been the subject of only a few publications [5–9]. Experimental data have been obtained from natural and synthetic single crystals. Kou and Seehra [5] and Seehra and Seehra [6] reported the variation in E_0 at temperatures lower than 400 K. They found that E_0 decreases smoothly and continuously on increasing the natural single-crystal temperature. These workers analysed their data by assuming a pyrite absorption edge due to an indirect transition. However, it has been shown [4] recently (both theoretically and experimentally) that the nature of the transition responsible for the optical absorption edge of pyrite is quite uncertain. In fact, several theoretical papers [10–15] have been published discussing the nature of possible electronic transitions of pyrite. Tsay et al [9] have published a linear relation between E_0 and T from 100 to 300 K obtained with synthetic single crystals. The values of E_0 are determined by applying the Moss rule and an indirect transition is also assigned to the optical absorption edge. However, this conclusion must be reconsidered in view of the relevant role played by defects and impurities which present photoresponse peaks below the absorption edge [16].

Other workers [7, 8] have discussed the experimental data [5, 6] by considering different empirical approaches.

In spite of the current importance of thin films, no information is available (as far as we know) on the temperature variation in E_0 for pyrite thin films. We now report that variation measured between 10 and 300 K in a pyrite thin film prepared by flash evaporation of pyrite powder [17, 18]. Experimental points show a well marked variation in E_0 with temperature, mainly in the high-temperature region. Two different functions for $E_0(T)$ have been tried to fit the experimental data: the empirical Varshni [19] formula and an expression, which has been previously used by other workers [20], where $E_0(T)$ is proportional to the Bose–Einstein statistical factor. This second formula allows us to calculate the average energy of the phonons involved in the process. The Raman spectrum of the same pyrite thin film has also been measured. The average energy of the active Raman modes agrees well with the value of the phonon energy as deduced from $E_0(T)$, which leads to the conclusion that mainly optical phonons are involved in the $E_0(T)$ behaviour.

2. Experimental details

A set of pyrite thin films has been prepared by flash evaporation of natural pyrite powder on glass substrates. Some of their optical and transport properties have been extensively studied and reported elsewhere [17, 18]. One of these evaporated films was selected in order to investigate the influence of temperature on its optical absorption edge. The x-ray pattern of the as-evaporated film showed pyrite and pyrrhotite structures but the sample became fully pyrite by a further anneal in a sulphur atmosphere at 623 K for 18 h. The x-ray diffraction spectrum obtained after annealing presented well defined pyrite peaks exclusively. The thin film thickness was 0.42 μm as determined with a Dektak profilometer. Its electrical properties were measured at RT by the four-contact Van der Pauw method and the following results were obtained: resistivity, 0.18 Ω cm; carrier mobility, 120 cm^2 V^{-1} s^{-1}, carrier concentration, 10^{17} cm^{-3}.

Optical absorption spectra of the film have been recorded at photon energies between 0.5 and 4.0 eV with a Cary spectrophotometer (model 2415). The sample was cooled to 10 K with the help of a He closed-circuit cryostat (CTI–Cryogenics model 21) and a temperature controller with 1 K resolution. Absorption spectra were obtained at a constant temperature in steps of 10 K when the temperature was increased from 10 to 300 K.

Raman spectroscopy of the film was carried out at RT with a Jarrel–Ash A.350 double monochromator with photon-counting detection with a photomultiplier. The 15 453 cm^{-1} line of a Kr ion laser was used as an exciting source of approximate power 400 mW.

3. Results and discussion

The optical absorption spectra of the sample at 10, 100 and 300 K are shown in figure 1. The absorption curves obtained at other temperatures are not given to avoid their inconvenient superposition. One can see that the optical absorption spectra do not change on passing from 10 to 100 K and that stronger variations appear on going to 300 K. The optical absorption coefficient at higher photon energies (about 2 eV) is almost temperature independent with a value of $(1.25–1.3) \times 10^5$ cm^{-1}. On the other hand, an absorption tail is shown by all the curves at lower photon energies. This tail has been attributed [18] to absorption by point defects present in the film in high concentrations.
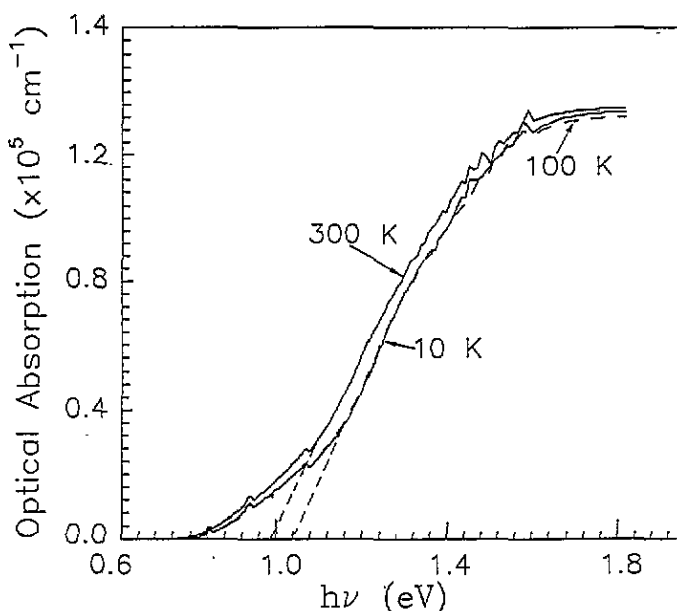
Figure 1. Optical absorption spectra of pyrite thin film at 10, 100 and 300 K. The broken straight lines are used to obtain E_0 (see text).

The pyrite absorption edge is assigned to a transition between the Fe 3d (t_{2g}) and e_g states [10, 12, 13, 21]. As we have mentioned above [4] and as shown by recent theoretical work [14], it is not yet clear whether a direct or an indirect transition is responsible for the optical absorption edge of pyrite. Probably the reason for this confusing situation is that the pyrite bands are rather flat [10–15] and not parabolic which makes [4] some simplified expression (such as $(\alpha h\nu)^n \propto h\nu - E_0$), commonly used with other semiconductors [22], useless. Then, we consider the optical absorption edge E_0 as that obtained from the linear extrapolation of the absorption curves in the maximum variation zone, as done by Sato [23] and ourselves [18] and shown in figure 1. This region, presented by all the curves in the same photon energy interval, has been fitted by a straight line using a least-squares program. The error obtained in E_0 is $\pm 5 \times 10^{-3}$ eV.

Influence of the measurement temperature on E_0 is shown in figure 2 by full circles. It can be seen that E_0 remains almost constant in the range 10–100 K and it decreases smoothly on passing from 100 to 300 K. This behaviour is quite parallel to that presented by natural single crystals previously investigated by other workers [5, 6]. Experimental values of E_0 change from 1.05 to 0.99 eV.

The temperature dependence of the semiconductor band gap is at present well explained by considering the lattice expansion produced on heating the sample and the electron–phonon coupling contributions. On the basis of the analysis of these two phenomena, different formal expressions and formulae have been proposed. O'Donnell and Chen [24] have analysed and compared the meaning of all these expressions. It can be concluded that, when small and meaningless differences are ignored, only two appear as really different: the empirical expression first proposed by Varshni [19] and used by many workers and the expression in which $E_0(T)$ is a linear function of the Bose–Einstein statistical factor [20]. These two approaches will be considered in the following analysis of our experimental data.
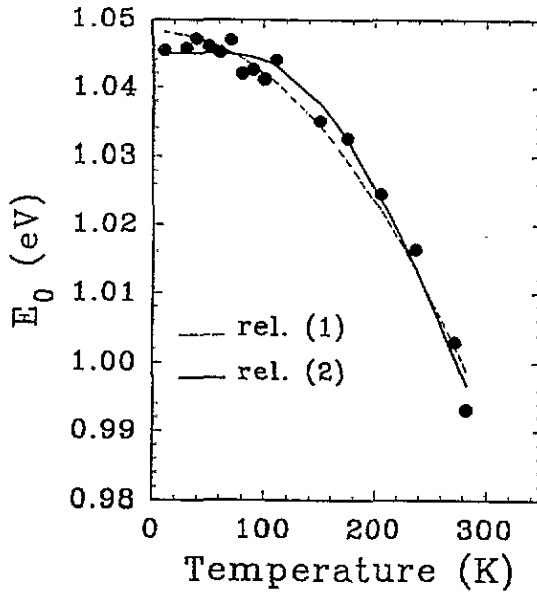
The empirical Varshni relation is

Figure 2. Optical absorption edge E_0 of a pyrite thin film as a function of temperature: ●, experimental points; – – –, data fitting to Varshni relation (1); ——, fitting by the Bose–Einstein relation (2).

$$E_0(T) = E_0(0) - a\frac{T^2}{T + b} \tag{1}$$

where $E_0(0)$ is the optical absorption edge at 0 K and a and b are empirical parameters which are determined by fitting experimental results. It is generally assumed that b represents the Debye temperature of the semiconductor. Fitting our experimental data to the Varshni formula is shown in figure 2 by the broken curve. The calculated curve closely resembles the general trend of experimental points but a discrepancy is clear at low temperatures. The experimental values of E_0 at temperatures below 100 K are almost temperature independent; however, the calculated curve shows a smooth but continuous decrease on increasing T.

Table 1. Parameters obtained from the fitting of experimental data in figure 2 with equations (1) and (2). $E_0(0)$ is the absorption edge at 0 K and Θ is the phonon average temperature involved in the variation in E_0 with T. The meaning of the other parameters is explained in the text.

	$E_0(0)$ (eV)	a (eV K^{-1})	b (K)	α (eV)	β (eV)	Θ (K)
Varshni equation (1)	1.048 ± 0.005	5.88	6×10^6			
Bose–Einstein equation (2)	1.045 ± 0.005	–	–	1.20	0.154	568 ± 10

Values of constants in (1) obtained from the experimental point fitting are given in table 1. The absorption edge at 0 K is $E_0(0) \simeq 1.048 \pm 0.005$ eV. This value is higher than that deduced by Kou and Sheera [5] (0.835 eV) and lower than that deduced by Tsay *et al* [9] (1.14 eV) by assuming an optical absorption edge due to an indirect transition.

The parameter b listed in table 1 appears to be about 6×10^6 K. As has been already noted, this parameter should mean the Debye temperature of pyrite. The values of b deduced

in [5] and [9] are −1395 K and 6 K, respectively. Therefore a very disappointing conclusion is reached at this point. Manoogian and Woolley [25] have made a detailed study of the temperature dependence of the energy gap in semiconductors. They have concluded that the parameter b in the Varshni equation can only be related to the Debye temperature Θ_D when the measurement temperature T is higher than Θ_D ($\Theta_D/T \ll 1$). Published data on the Debye temperature of pyrite are 610 K [26], 703 K [27] and 761 K [8], i.e. much higher than the temperatures investigated in this paper and in [5] and [9]. Therefore, one should conclude that the large discrepancies in b appear as a consequence of the lack of understanding of the meaning of b at low temperatures.

The second relation between E_0 and T which we shall consider is

$$E_0(T) = \alpha - \beta \left(1 + \frac{2}{\exp(\Theta/T) - 1}\right) \qquad (2)$$

where β represents the strength of the electron–phonon interaction and Θ is the average temperature of phonons taking part in the process. Equation (2) has been widely used to analyse the energy gap temperature dependence in several semiconductors (Ge [20], Si [28] and GaAs [24, 29]). Fitting our experimental data with (2) is shown by the full curve in figure 2. It can be seen that the calculated E_0 remains constant at low temperatures. The absorption edge at 0 K is given by the difference $\alpha - \beta$ in (2). Values of $E_0(0)$, α and β are given in table 1. We have obtained $E_0(0) = 1.045$ eV, very similar to the value obtained from the Varshni formula. On the other hand, Θ, the average temperature of phonons, appears to be 568 K (table 1). This very high phonon temperature suggests that phonons contributing to the absorption edge variation are mainly optical phonons. In order to check the reliability of this qualitative conclusion we have recorded a Raman spectrum of the pyrite thin film. The Raman spectrum shown in figure 3 has been obtained without specifying the entrance and exit light polarization directions. Three peaks appear at 341, 377 and 427 cm^{-1}. They correspond to the five Raman active modes which are characteristic of pyrite observed in single crystals (343, 350, 377, 379 and 430 cm^{-1}) [30–33], although two of them (at 343–350 and 377–379 cm^{-1}) are not resolved. An average value of the phonon temperature can be deduced by approximating the relative weight of each frequency to the corresponding area under the peak in figure 3. We have obtained an average phonon temperature of 541 K. Published data [33], calculated and observed by Raman and infrared spectroscopies, on the mean LO and TO phonon vibration frequencies in pyrite are 558 K and 543 K, respectively. They are in very good agreement with the average value obtained from our spectrum. We can now conclude that the average phonon temperature (568 K) obtained on fitting our experimental data of figure 2 to equation (2) indicates that the phonons which contribute to the E_0 variation with T are mainly optical phonons.

We have emphasized that the electronic structure of pyrite has not been intensively investigated and that a reduced number of band-structure calculations are available [10–15]. They agree qualitatively in many aspects although there are significant quantitative variations in regard to the band separation of pyrite. From a qualitative point of view, one can assume [14] that the absorption of low-energy (less than 1.2 eV) photons is associated with a weak indirect transition and that the higher-energy (1.2 eV or above) photon absorption is related to a direct transition.

In this scheme we can tentatively suggest that the optical absorption edge E_0 analysed in this paper should be closely connected to the direct transition. On the other hand, an analysis of the indirect transition in pyrite thin films seems to be difficult (if not impossible at present) owing to the strong absorption caused by point defects at low photon energies.
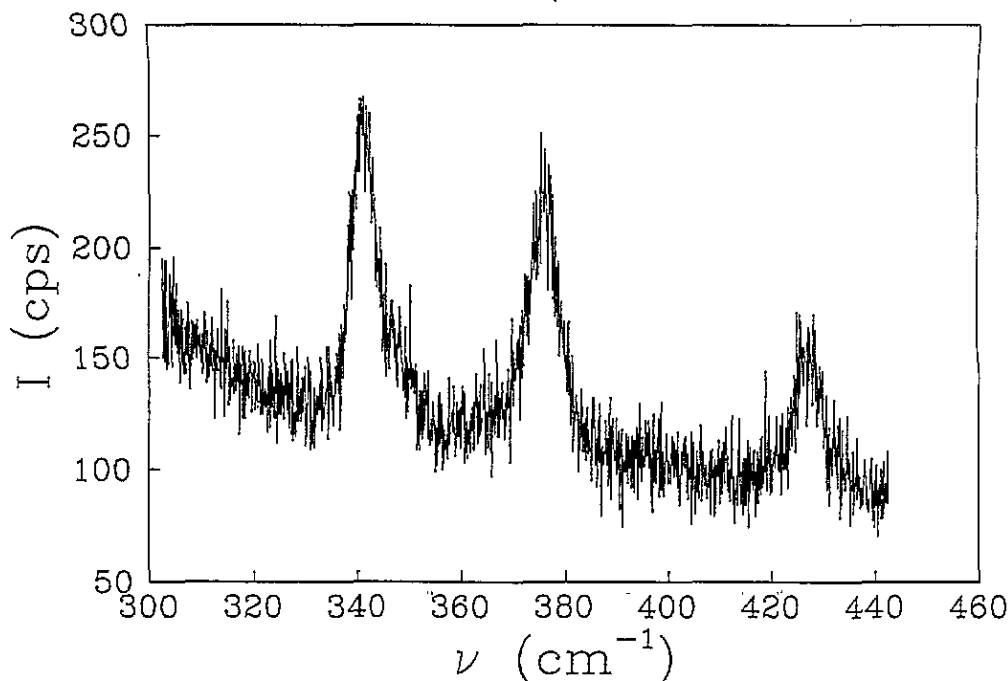
Figure 3. Raman spectrum of the polycrystalline thin film obtained with unpolarized light.

4. Conclusions

We have investigated for the first time the influence of temperature on the optical absorption edge of pyrite thin films. From the fit of the experimental data to equation (2) (a function of the Bose–Einstein statistical factor) and from the Raman spectrum of the same film we conclude that the Raman optical active modes are mainly responsible for the temperature variation of the absorption edge. The shape of the experimental E_0 versus T curve obtained with thin polycrystalline films is very similar to that shown by pyrite natural single crystals.

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