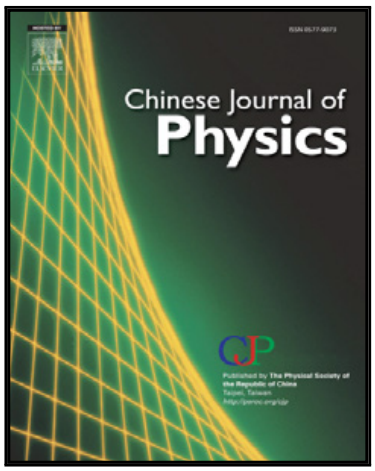

Photoluminescence of polycrystalline $CuIn_{0.5}Ga_{0.5}Te_2$ thin films grown by flash evaporation

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Highlights

- Layers were deposited by flash evaporation from $CuIn_{0.5}Ga_{0.5}Te_2$ powder.
- The chalcopyrite structure of $CuIn_{0.5}Ga_{0.5}Te_2$ material is confirmed by X-ray.
- Optical measurements yielded a band gap of 1.27eV.
- PL study revealed that the radiative emissions arise from (FB) and (DAP) recombination.

Photoluminescence of polycrystalline $CuIn_{0.5}Ga_{0.5}Te_2$ thin films grown by flash evaporation

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Abstract

Polycrystalline $CuIn_{0.5}Ga_{0.5}Te_2$ films were deposited by flash evaporation from ingot prepared by reacting, in stoichiometric proportions, high purity Cu, In, Ga and Te elements in vacuum sealed quartz . The as-obtained films were characterized by X ï ray diffraction (XRD), transmission electron microscopy (TEM) combined with energy dispersive spectroscopy (EDS). XRD and TEM results showed that the layer has a chalcopyrite-type structure, predominantly oriented along (112) planes, with lattice parameters *a = 0.61 nm and c = 1.22 nm*. The optical properties in the near - infrared and visible range 600 - 2400 nm have been studied. The analysis of absorption coefficient yielded an energy gap value of 1.27 eV. Photoluminescence analysis of as-grown sample shows two main emission peaks located at 0.87 and 1.19 eV at 4 K.

Keywords: Chalcogenides; Optical materials; Semiconductors; Thin films; transmission electron microscopy.

1. Introduction

The development of ternary semiconductor structure of ABC_2 chalcopyrite-type is mainly focusing on sulfur-based compounds or selenium. Except the research works reported by Yẽlmaz et al. [1] and Yandjah et al. [2] devoted to the study of annealed Cu (In, Ga)Te_2 thin films and the investigation of bulk samples [3], no significant reports in the literature related to the Cu (In, Ga)Te_2 quaternary tellurides can be found so far. Numerous experimental results showed that the chemistry of semiconductor compounds plays a fundamental role in the understanding of their properties [4-8]. In particular, the intrinsic point defects are likely related to the nature of the materials and essentially control their optoelectronic properties. The photoluminescence is known to be a powerful and non-destructive technique as well as very sensitive to the semi-conductor characteristics (concentration and defects energy levels).

Although, it is well-known that $CuInTe_2$ single crystal obtained by different methods is found to be a p-type [9,10]; n-type conduction has been also obtained when the material is annealed in an indium atmosphere [11]. It has a band gap of 1.06 eV at 0 K [12-14] and a value close to 0.96 eV at room temperature [15,16]. The reported photoluminescence spectrum exhibits many radiative transitions [12,13]: (i) the emission at 1.05 eV is associated with the free exciton recombination; (ii) the transition occurring in the energy range 1.03 - 1.05 eV is due to donors or acceptors bound excitons recombination; (iii) however, the emissions in the energy range 1.02-1.02 eV are assigned to donor - acceptor recombinations.

Moreover, $CuGaTe_2$ ternary compound has a p-type conduction and a direct energy band gap Eg = 1.22-1.24 eV at room temperature and close to 1.30 eV at 0 K [17-19]. A value of 1.35 eV was also reported for polycrystalline thin films [16]. Krustok et al. [19] carried out photoluminescence measurements on $CuGaTe_2$ single crystal obtained by the vertical Bridgman method. The PL spectrum consisted of two regions: three transitions namely E_1, E_2 and E_3 are present at high energy; however a single low energy transition labeled D_o is shown.

The measurement of several direct and indirect gaps was determined for this material [17-22]. In this research work, we report on the synthesis, structural and optical characterizations of a-grown $CuIn_{0.5}Ga_{0.5}Te_2$ absorber layers.

2. Experimental Part

Polycristalline $CuIn_{0.5}Ga_{0.5}Te_2$ films were grown by flash evaporation onto pre-cleaned glass substrates. Substrate temperature was set at 400°C. The structure of the films was investigated by X-ray diffraction (XRD) using diffractometer equipped with Cu radiation source (λ_{Cu}=1.5418Å). For transmission electron microscopy (TEM) observations, the material was evaporated on carbon films supported by Ni grids directly on the substrate. TEM and energy dispersive spectroscopy (EDS) analyses were carried out using a JEOL2010CX TEM operating at 200 kV. For small-area-composition measurements, a spot size of 25 nm was used. Optical properties of the as-prepared layers were characterized by UV-visible absorption spectroscopy recorded with a Perkin Elmer Lambda 950 UV-Vis spectrometer. The carrier type films were determined using the hot probe technique. All layers present a p-type conductivity. The values of conductivity at room temperature were estimated to be in the range $1\text{-}10^2$ $(\Omega cm)^{-1}$. Photoluminescence (PL) measurements were carried out between 4.2 and 50 K. An argon ion (Ar^+) laser, with 514.5 nm line in the excitation intensity range from 20 to 650 mW, was used as excitation source. Emission spectra were analyzed using a Jobin-Yvon HR1000 monochromator with a liquid-nitrogen - cooled North Coast EO-817 germanium detector.

3. Results and Discussion

3.1 Crystal Structure Analysis

Figure 1 displays X-ray diffraction patterns of $CuIn_{0.5}Ga_{0.5}Te_2$. Figure 1a shows reflections from the powder corresponding to the chalcopyrite structure (card No. ¸ 34 ï 1499), with a

predominently intense peak a along (220/204) direction. Some reflections of an additional binary phase are detected (circular dots). Comparing the interplanar distances of these reflections with JCPDS cards, the latter reflections can be associated to the tetragonal structure of Cu_2Te_7 (card# 29 - 575).

Figure 1b shows the X-ray diffraction profile of $CuIn_{0.5}Ga_{0.5}Te_2$ film deposited onto glass substrate at temperature T_s = 400°C. The layer is polycrystalline single tetragonal phase of X-type exhibiting a strong preferred orientation along (112) plane. The calculated cell parameters are: *a= 0.61 nm and c=1.22 nm.*

3.2 TEM Analysis

The bright-field TEM image of the layer is shown in Figure 2. The crystal structure of the deposited film is analyzed via selected area electron diffraction (SAED) (see inset Figure 2). The presence of $CuIn_{0.5}Ga_{0.5}Te_2$ phase with chalcopyrite like-structure is confirmed in the SAED pattern by the presence of rings corresponding to (112), (204, 220) and (116, 312) planes. The derived parameters (*a= 0.57 nm, c = 1.34 nm)* are in good agreement with the values calculated from XRD data.

The combined STEM/ EDS analysis of the film revealed that it is nearly stoichiometric and the determined weight % elemental composition of Cu, In, Ga and Te is 20.3, 11.1, 13.6 and 55.0 %, respectively. The obtained values are slightly different from the ingot quantitative analysis at% (Cu = 24.17, In = 10.64, Ga = 11.93 and Te = 53.26%). This difference arises from the evaporation conditions.

Moreover, the nanoanalysis of $CuIn_{0.5}Ga_{0.5}Te_2$ crystal is also determined by EDS analysis (Figure 3). The composition of the studied evaporated thin film is found to be 25.5, 19.1, 6.5, 48.9 at% for Cu, In, Ga and Te, respectively. The presence of C and Ni peaks are due to the grid substrate.

3.3 Optical Properties

3.3.1 Transmission and Reflection Analyses

The optical absorption coefficient α of $CuIn_{0.5}Ga_{0.5}Te_2$, is calculated using the relation (1) [23]:

$$\alpha = -\frac{1}{t} Ln\left(\frac{T}{(1-R)^2}\right) \qquad (1)$$

where t is the thickness of the crystal; T and R are the transmission and reflection (%) coefficients (Figure 4), respectively. The thickness (t = 2.7 µm) of the obtained film was calculated from the transmission fringes [24].

The absorption obeys the relation of the form $\alpha h\nu = \sqrt{h\nu - Eg}$, which is valid for direct transitions [25]. The band gap is determined from Tauc's plot [26] $h\nu$ versus $(\alpha h\nu)^{1/n}$, where the value of n (n = 1/2) gives the best linear fit in the band edge region. The optical energy band gap of $CuIn_{0.5}Ga_{0.5}Te_2$ is estimated by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The estimated optical band gap is about 1.27 eV (Figure 5).

3.3.2 Photoluminescence Analysis

PL measurements are performed on $CuIn_{0.5}Ga_{05}Te_2$ at various temperatures and laser excitation densities. The recorded spectra are presented in Figure 6. It is observed that the first peak appearing at 0.87 eV shifts towards lower energies with increasing temperatures. Additionally, its intensity decreases drastically while the full width at half-maximum (FWHM) of the emission band increases with temperature. Furthermore, when the laser power is raised, the peak position shifts towards higher energies. This behaviour is associated with a donor-acceptor pair (DAP) recombination [3,19].

However, the second radiative prominent peak at 1.19 eV nearly does not change with increasing excitation power. The latter emission is rather assigned to free-to-bound (FB)

recombination. Since the as-prepared film has a p-type conduction as determined from Hall effect measurements at room temperature (p = $2x10^{16}cm^{-3}$), we suggest that the transition is associated with (FB) recombination involving a donor defect level and the valence band.

In a FB recombination, the energy position is given by the relation (2):

$$h\nu = E_g(0) - E_D + \frac{1}{2}k_B T \qquad (2)$$

with $E_g(0)$ the gap energy at 0K and k_B, the Boltzmannôs constant. This last value is determined from the variation of the direct gap [27] with temperature using the empirical relation (3) [28]:

$$E_g(T) = E_g(0) - \frac{AT^2}{B+T} \qquad (3)$$

The derived value of band gap from the optical measurements is E_g (300K) = 1.27 eV. The calculated $E_g(0)$ is 1.37 eV when A = $4.8x10^{-4}$ eV/K and B = 200 K. The estimated donor ionization energy E_D [29] is 170 meV.

The acceptor level energy E_A, is then calculated using the well-known formula for the donorï acceptor transition (4) [30]:

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{4\pi\varepsilon\varepsilon_0 r}. \qquad (4)$$

where E_g is the band gap energy, E_A and E_D are the acceptor and the donor levels, ε is the dielectric constant and ε_0 is the vacuum permittivity and r is the separation of DAP. From the radiative emission 0.90 eV occurring at 10 mW and the above equation, one can determine the value of E_A (E_A = 295 meV).

The above defect nature assignment is supported by the variation of the PL intensity (I) of the peaks as a function of the excitation power (P) according to the classical equation $I = CP^k$ (C is a constant and k represents the radiative recombination mechanism [31]).

A superlinearity is observed in the relation between these two parameters (Figure 7). The k factor is equal to 0.93 and 0.79 for the emissions at 0.87 and 1.19 eV, respectively. Thereby, the emissions lines are attributed to either free-to-bound (FB) or donor-acceptor pair (DAP) recombinations since k is lower than 1.

4. Conclusion

$CuIn_{0.5}Ga_{0.5}Te_2$ films were successfully grown by flash evaporation. Both XRD and TEM analyses confirmed the formation of $CuIn_{0.5}Ga_{0.5}Te_2$ chalcopyrite-type structure meanwhile EDS analysis showed a slight deviation from the expected stoichiometric elemental chemical composition. Moreover, transmission and reflection optical measurements yielded to a band gap value of 1.27 eV. On the other hand, temperature and laser power studies of PL revealed a linear behavior leading to the conclusion that the dominant emissions arise from free to bound and donor acceptor recombination.

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Figures Captions

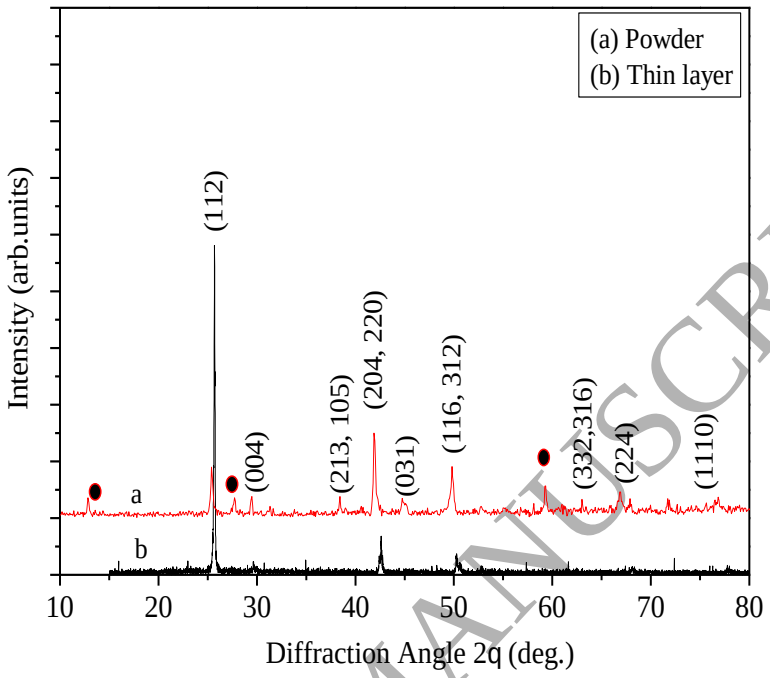

Figure 1. XRD diffraction patterns for powder and thin film deposited onto glass substrate. Cu_7Te_5 phase is designed by circular dots.

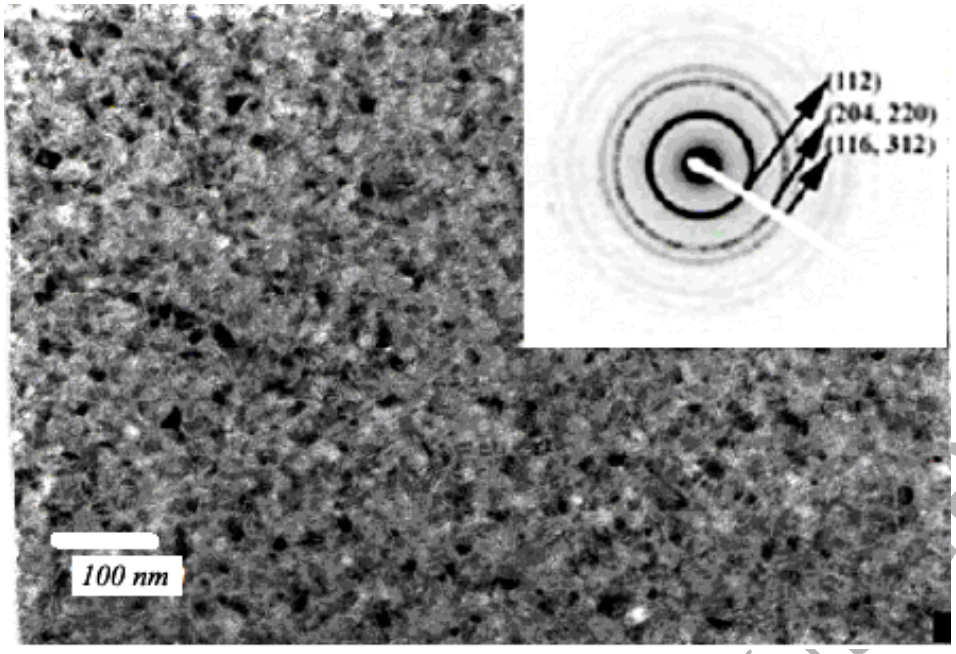

Figure 2. Bright field TEM image and the corresponding selected area electron diffraction pattern.

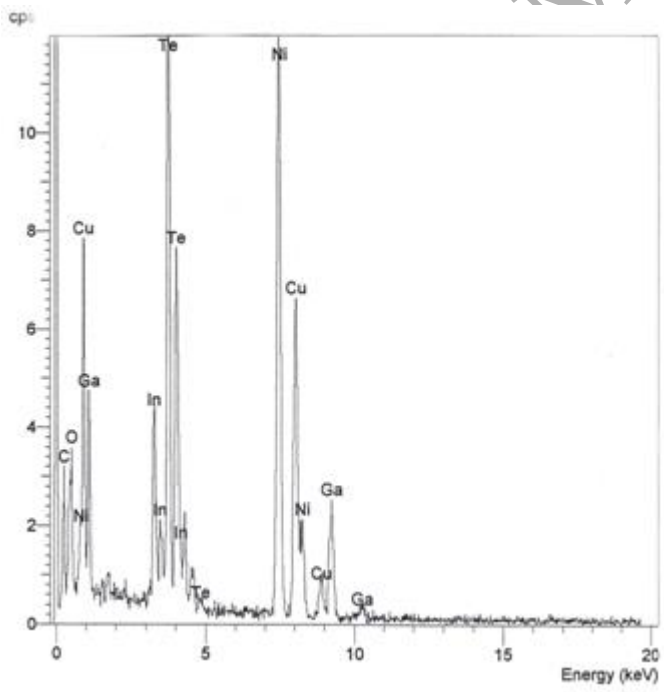

Figure 3. EDS spectrum of the selected TEM region.

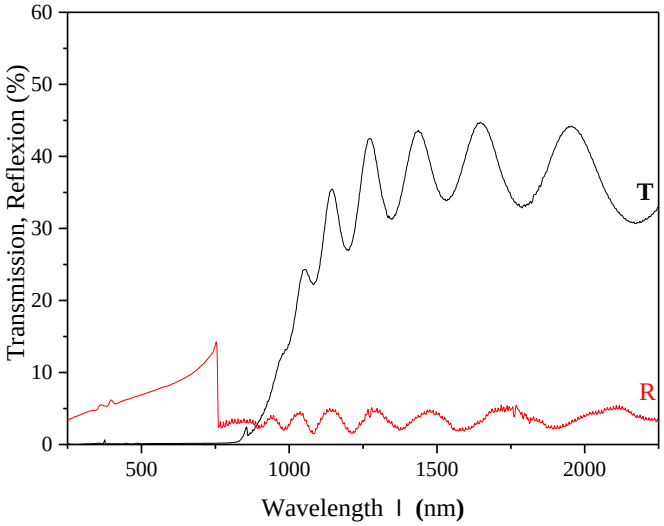

Figure 4: Transmission and reflection (%) as a function of wavelength measured at 300K.

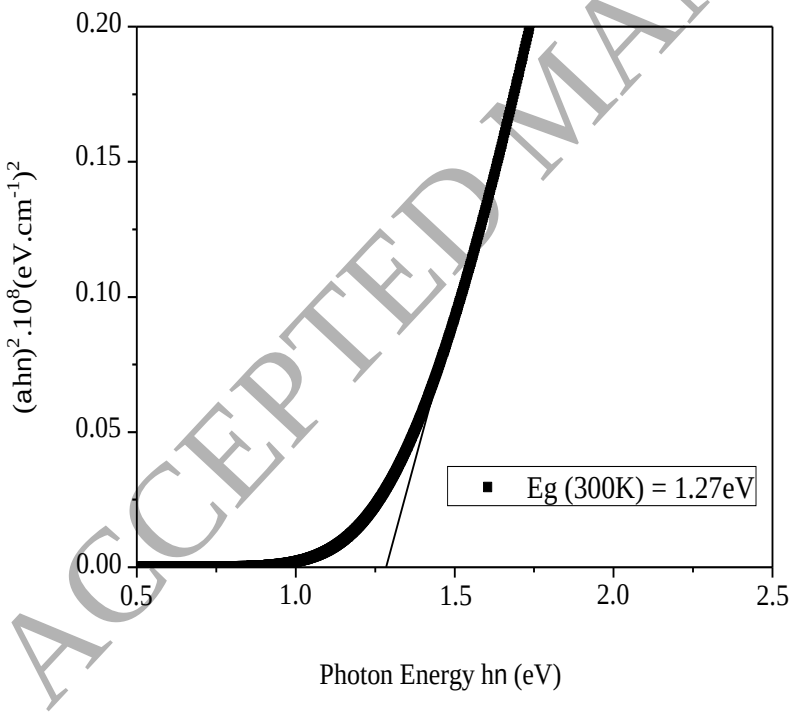

Figure 5. $(ahn)^2$ vs energy (hn) of $CuIn_{0.5}Ga_{0.5}Te_2$ thin film.

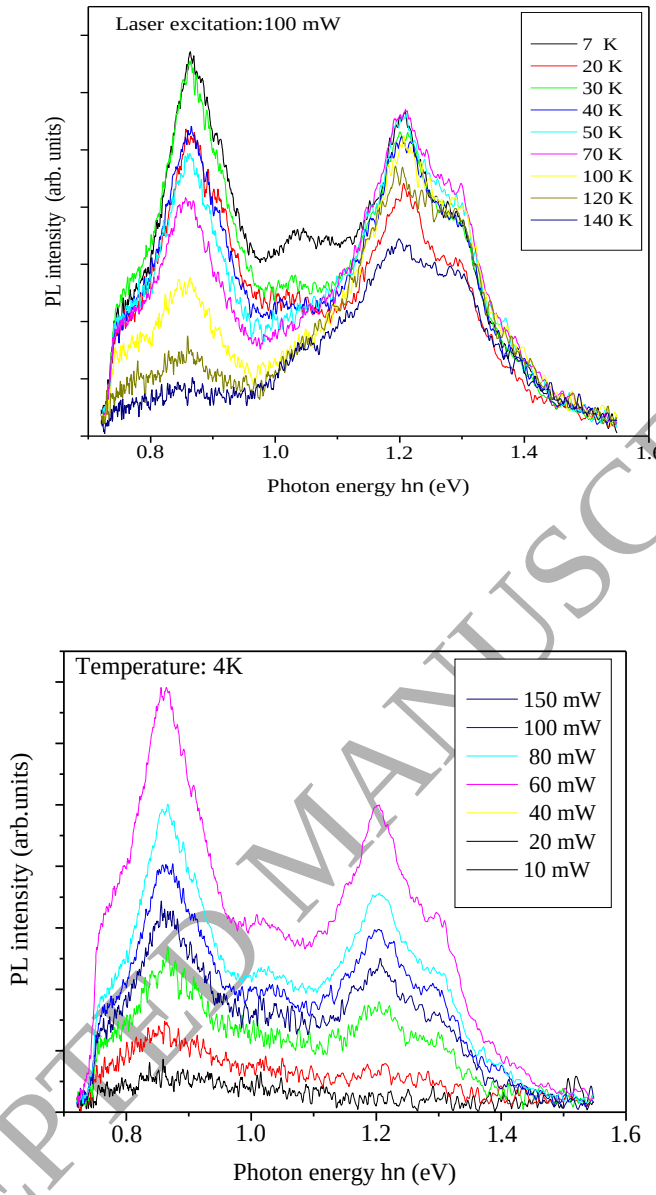

Figure 6. Dependence of $CuIn_{0.5}Ga_{0.5}Te_2$ PL spectra with temperature and excitation power.

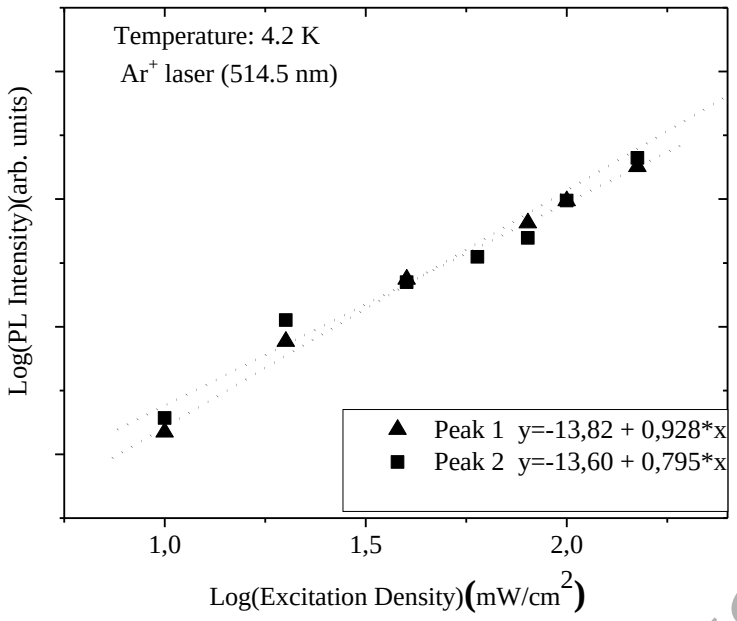

Figure 7. Emission intensity variation as a function of excitation power.