Crystalline Structure, Photoluminescence and Optical Absorption of $\beta - Ga_2S_3$ Crystals

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***Abstract* — Crystalline structure, photoluminescence and optical absorption of Ga_2S_3 in form of monocrystalline layers at 78K and 293K were investigated. A indirect optical bandgap of 2,94 eV and 3,078 eV was found for monocrystalline samples, and of 3,149 eV and 3,393 eV for direct optical band gap, at 293K and 78K, respectively. The photoluminescence spectrum of monocrystalline layers at 78K consists of three main bands peaked at 2,04 eV, 1,84 eV and 1,66 eV. Structural native defects create deep recombination and electron capture levels within the Ga_2S_3 band gap.**

***Index Terms* — III-VI layered semiconductors; Ga_2S_3; Optical properties; Photoluminescence.**

I. INTRODUCTION

The recent growing interest in III-VI layered semiconductors, a class of yet unexplored materials, is determined by their important role in the academic research, as well as by a wide range of technological applications (optoelectronic, photonic, spintronic devices, interferometric devices, etc.) [1-6].

Gallium sulfide (Ga_2S_3) is a member of III-VI semiconductor family, which was less investigated so far. One of the main reasons is presence of large native defect concentrations, determining rather low electrical conductivity of its samples. Ga_2S_3 is a wide band gap semiconductor showing marked photoconductivity in the blue-violet spectral range [7]. Peculiarities of its structural defects, e.g. presence of vacancies in the cationic subnetwork (a more general feature of III_2VI_3 crystals) [8], determine common physical properties for both Ga_2S_3 single crystals and nanocrystals. Due to specific bonding structures, Ga_2S_3 single crystals show easy cleavage in direction perpendicular to their C-axis. $\beta - Ga_2S_3$ polymorph is characterized by a würtzit-type structure, with parameters $a = 3{,}678$ Å and $c = 16{,}018$ Å [9, 10]. Owing to its peculiar characteristics, Ga_2S_3 is considered as perspective material for divers technological appllications: as passivation layer [4, 5, 11], optical and optoelectronic applications [12, 13], photovoltaic structures [14, 15], as well as full-color display [16, 17].

One of the first studies on the photoluminescent (PL) properties of Ga_2S_3 polycrystals is reported in [18], where general characteristics of PL bands are analysed. More recent papers [19-21] address photoluminescence of undoped and Mn-, Ag-, Cu-, Ge and Sm-doped Ga_2S_3 single crystals (especially, α polymorph).

In the present paper, crystalline structure, PL and optical properties of Ga_2S_3 in form of monocrystalline layers are examined.

I. EXPERIMENTAL DETAILS

Optical absorption and PL measurements have been performed on monocrystalline (bulk) layers of Ga_2S_3, were obtained using I_2 vapor transport at normal atmospheric pressure. As the primary source was used polycrystalline Ga_2S_3 synthesized from basic component of Ga (5N) and S (4N) taken in stoichiometric quantities. The primary material (polycrystalline Ga_2S_3) was synthetic in thick-walled quartz ampoules (4 mm) at temperature 1300°C for 12 hours. Ga_2S_3 polycrystals sublime at temperatures of $t \geq 550°C$ fact which allowed us to obtain monocrystals of Ga_2S_3 at temperature of 720°C. Source temperature was 750°C.

Optically homogeneous monocrystalline Ga_2S_3 layers with area $2 \div 8\ mm^2$ and thickness between ~50 μm and $1 - 2\ mm$ it were used at t optical transmittance measurement.

Crystalline structure of examined materials was confirmed by X-ray diffraction (XRD) studies, performed with a XRD 6000 Shimadzu X-ray diffractometer (Cu K_α radiation $\lambda = 0{,}154056\ nm$) and the characteristic lines indicating the presence of $\beta - Ga_2S_3$ were registered.

Absorption coefficient α in the region of the absorption band edge of Ga_2S_3 monocrystals was calculated using the obtained results at measuring the R reflection and transmission t coefficients from the relation [22]:

$$\alpha = \frac{1}{d} ln \frac{(1-R)^2 + [(1-R)^4 + 4R^2T^2]}{2T} \quad (1)$$

where d is the thickness of parallel plane plates of Ga_2S_3.

From (1) formula follows that for absorption coefficient measurement error does not exceed the error amount at measuring the ΔR reflectivity $d(\Delta d)$ thickness and transmittance Δt measurements is needed minimum of three samples with thickness is between $0{,}01 \div 5\ mm$. For this reason for the absorption measurements in of the absorption band edge region were prepared plates of Ga_2S_3 with the thickness of $87\ \mu m$, $190\ \mu m$ and $3200\ \mu m$ with a surface area of $\sim 2\ mm^2$.

PL of Ga_2S_3 at temperatures $78K$ and $293K$ was investigated on monocrystalline layers with optical axis (C_6) perpendicular to the sample surface. Before optical and/or PL measuremnts, Ga_2S_3 samples have been annealed for $4\ h$, in vacuum at $400 - 420$°C, in order to remove the excess of iodine.

The spectral characteristics of the optical absorption and PL have been recorded by a spectrophotometric set-up including a MDR-2 monochromator with diffraction grating ($1200\ mm - 1$ and $600\ mm - 1$). In measuring optical absorption the irradiation was performed with an incandescent lamp. The excitation of PL was performed by using the monochromatic radiation provided by a N_2 laser ($\lambda = 337\ nm$). The density of the exciting radiation was varied by using neutral density filters (thin Pt films onto amorphous quartz).

II. RESULTS AND DISCUSSION

Figure1 shows the XRD diffractogram at 2θ range from $10°$ to $120°$ of Ga_2S_3 crystals obtained by I_2 transport. 2θ angles of diffraction lines with relative intensity greater than 500 are entered in the table. As we can see from Figure1 and the table once with Ga_2S_3 phase diffraction lines are presented low intensity diffraction lines which in [23] are identified as X diffraction lines of α-Ga_2S_3 phase.After Bragg diffraction angle values were calculated lattice parameters which are equal to $a = 11{,}15$ Å; $b = 6{,}36$ Å; $c = 7{,}06$ Å; and $\beta = 120^o56'$. These parameters correspond to $\beta - Ga_2S_3$ phase. This phase is stable both in single solid crystals and the nano-particles [24].

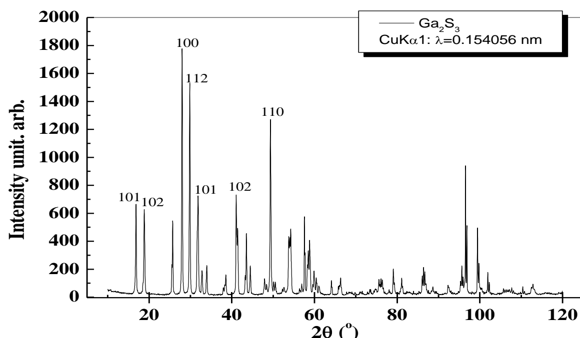

Fig. 1. XRD Difractograma of Ga_2S_3 cristals

Table Difraction angles, intensity and respective Miller parameters, for Ga_2S_3 crystals

Nr. crt.	2θ, °	I, unit. arb.	h k l	crystalline lattice
1	16,86	664	1 0 1	hexagonal
2	18,84	626	1 0 2	
3	28,00	1777	1 0 0	
4	29,86	1530	1 1 2	
5	31,86	625	1 0 1	
6	41,08	731	1 0 2	
7	49,36	1271	1 1 0	

Ga_2S_3 crystals are transparent in the spectra's visible region. In Figure 2 are represented absorption spectra calculated from t transmission and R reflection measurement of Ga_2S_3 plates with the formula (1).

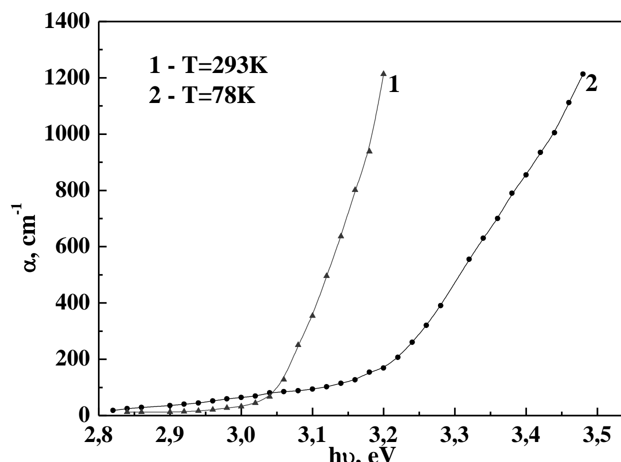

Fig. 2. Absorption spectra of Ga_2S_3, at temperature of 293K (curve 1) and 78K (curve 2).

The absorption band edge at $293K$ temperature is at $h\nu \sim 3{,}03\ eV$ and $3{,}2 eV$ at $78K$. $\frac{\Delta\alpha}{\Delta h\nu}$ slope small relation both at $293K$ temperature and $78K$, respectively $\frac{6200\ cm^{-1}}{eV^{-1}}$ and $\frac{3150\ cm^{-1}}{eV^{-1}}$, indicates about presence in this material of indirect optic transitions.

In case of indirect optic transitions the photons absorption process occurs with photons' emission and absorption. The optical photons' energy in Ga_2S_3 crystals is $\omega_{LO} = 431\ cm^{-1}$ and $\omega_{TO} = 365\ cm^{-1}$ [25]. As the thermic energy at normal temperature is $E_T = 0{,}025\ eV$ and is much lower than medium energy of optical photons the indirect optical transitions in Ga_2S_3 can be realized with photons emission. So, in the approximation $h\nu_f \gg kT$ the spectral dependence of absorption coefficient at indirect optical transitions cu photons energy emission α_e^i is given by the equality [26]:

$$\alpha_e^i \cdot h\nu = A\left(h\nu - E_g^i - h\nu_f\right)^2 \qquad (2)$$

where $h\nu$, $h\nu_f$ photons' energy and photons medium energy, k –Boltzman constant, T – absolute temperature, A – the parameter determined by the indirect optical transitions' probability.

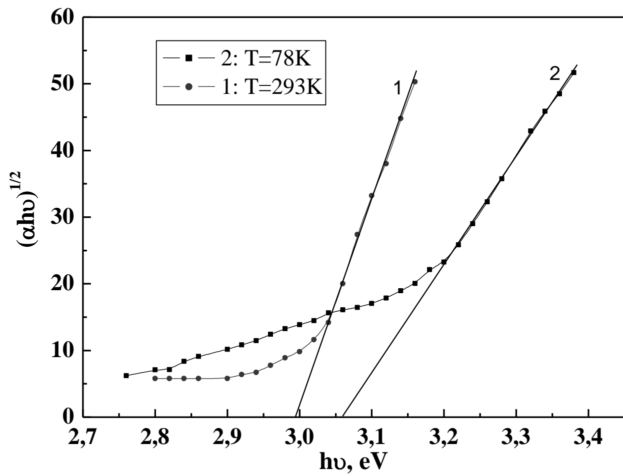

Fig. 3. Spectral dependences of the absorption coefficient $(\alpha h\nu)^{1/2}$ Ga_2S_3 crystals at $293K$ and $78K$ temperature.

The spectral dependences of absorption coefficient $\alpha_e^i \cdot h\nu$ of Ga_2S_3 crystals obtained by transport through I_2vapors from $293K$ and $78K$ temperature are presented in Figure 3.

We can see that in the interval of absorption coefficients $60 < \alpha < 700\ cm^{-1}$ at $T = 293K$ and $130 < \alpha < 700\ cm^{-1}$ at $T = 78K$ the experimental results are well described in Figure 2. Through linear segment exploitation at $\alpha_e = 0$ was determined the energetic interval $E_g^i - h\nu_f$ equal with $2{,}99\ eV$ and $3{,}078\ eV$ respectively at $T = 293K$ and $T = 78K$.

The absorption band edge of Ga_2S_3 crystals at absorption coefficients $\alpha \geq 700\ cm^{-1}$, as we can see in Figure 4 (curve 1, 2) can be approximated with an relation like [27]:

$$\alpha \cdot h\nu = A^x\left(h\nu - E_g^d\right)^m \qquad (3)$$

where A^x – a term determined by the direct optical transitions probability from the valence band maximum in the minimum of conduction band, E_g^d–the direct band gap width.

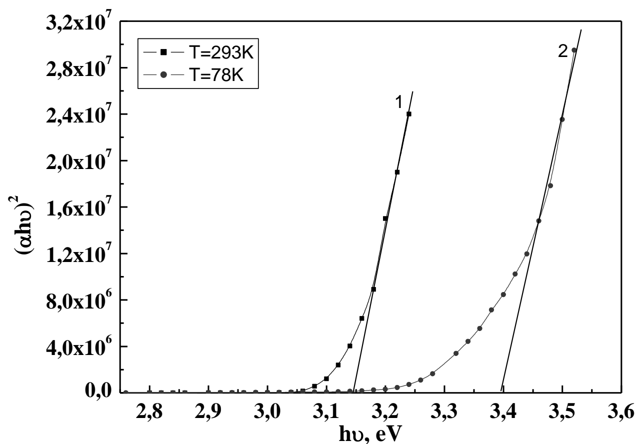

Fig. 4. The spectral dependences of absorbtion coefficient $(\alpha h\nu)^2$ of Ga_2S_3 crystals at temperature of $293K$ and $78K$.

Power factor "m" as shown in Figure 4 (curve 1, 2) equals ½ from the size corresponding direct optical transitions allowed.

Through the linear segment exploitation of $(\alpha h\nu)^2 = f(h\nu)$ at $\alpha \geq 0$ dependence was determined the direct gap band width E_g^d equal with $3{,}149\ eV$ and $3{,}393\ eV$ at sample temperature of $293K$ and $78K$ respectively.

In the following the results concerning PL properties of monocrystalline Ga_2S_3 layers with the thickness of $58\ \mu m$ are analyzed. The PL spectra of monocrystalline Ga_2S_3, at $78K$, for three different exciting levels ($800\ W/cm^2$, $500\ W/cm^2$, and $60\ W/cm^2$), are presented in Fig. 1.

As can be observed from this figure, the PL spectrum covers a wide spectral range, from $1{,}5\ eV$ to $3{,}1\ eV$. Its high-energy tail practically coincides with the absorption fundamental edge of the sample [28]. The PL intensity slowly increases in the region by the vicinity of the absorption edge. This feature can be explained by high probability of non-radiative transitions between electron states localized in the band tails, as mentioned above.

At photon energies below $2{,}5\ eV$, the PL shows a rapid increase, regardless of the exciting beam density, and reaches its maximum at $(1{,}84 - 1{,}95)\ eV$. This PL band arises from superposition of three photoluminescence bands, located at $2{,}04\ eV$, $1{,}84\ eV$ and $1{,}65 - 1{,}67\ eV$, respectively. As can be observed from comparison of curves *a, b* and *c* (Fig. 1), the intensity of this band depends non-monotonically on the exciting radiation density. The particularities by $2{,}39\ eV$ and $2{,}74\ eV$ (Fig. 1) are determined by the presence of two acceptor levels localized at $0{,}92\ eV$ and $0{,}47\ eV$ above the valence-band edge, respectively [7].

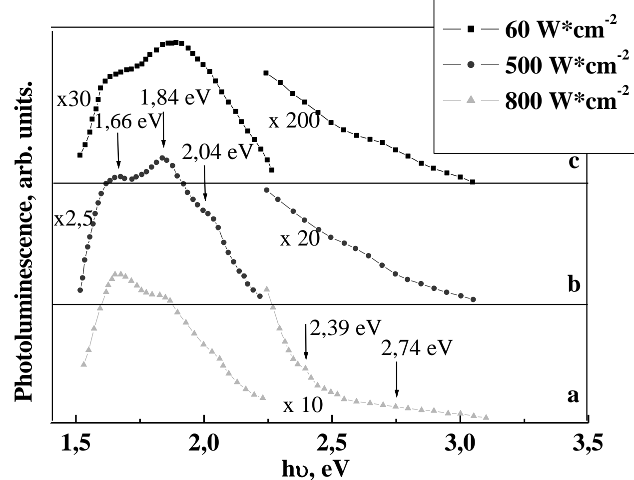

Fig. 5. Photoluminescence spectra of monocrystalline Ga_2S_3 layers ($d = 58\ \mu m$)at 78 K. Excitation level: (a) $800\ W/cm^2$, (b) $500\ W/cm^2$, and (c) $60\ W/cm^2$).

For the PL bands of monocrystalline Ga_2S_3 layers, the dependence of photoluminescence intensity, *L*, on the excitation density, *W*, is showed in figure 5. As can be observed from this figure, the *L*(*W*) dependence can be described by a power-law type function

$$L \propto W^p \qquad (4)$$

where the index *p* characterizes the PL kinetics in the respective bands. As can be found from figure 6, the power index, *p*, is equal to 0,9 and 1,0 for PL bands peaked at $2{,}04\ eV$ and $1{,}84\ eV$, respectively. The obtained values, equal or close to one, are indicative of a *first-order luminescence kinetics* for these bands. For the band located at $1{,}66\ eV$, the index *p* is equal to 1,4,

therefore it can be stated that this band has a recombination character.

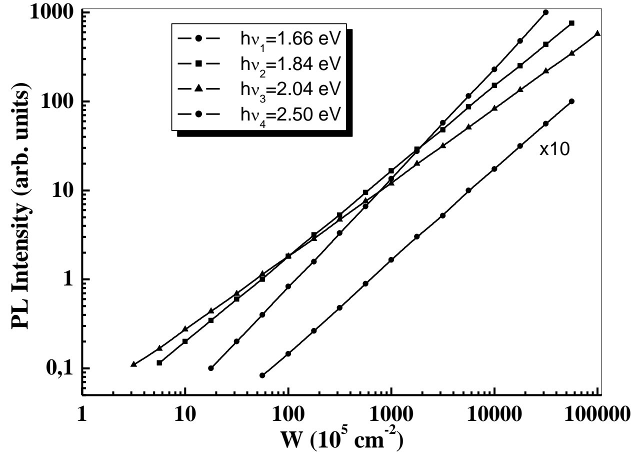

Fig. 6. Dependence of photoluminescence intensity, L, on excitation power density, W, for monocrystalline Ga_2S_3 layers.

As can be seen in figure 7 (curves 1 and 2), the PL intensity of the two bands shows an overall decrease at increasing temperature from $78K$ to room temperature. For the band located at $1,66\ eV$, the PL intensity displays a decreasing tendency in the temperature range $78K < T < 145K$, and only at temperatures $T > 150K$ the thermal quenching of the PL emission is registered. Unlike this, the temperature dependence of the PL intensity for the band peaked at $1,84\ eV$ is characterized by two linear parts with quite different slopes, which can be described by [4]

$$L(T) = \frac{L(0)}{1+\alpha\exp(-\Delta E/kT)} \tag{5}$$

where $L(0)$ denotes the PL intensity at 0K, ΔE is the activation energy of thermal quenching of the respective PL band, α is a constant depending on the compound nature, and k is Boltzmann's constant. The value of ΔE can be determined from the slope of $ln[L(0)/L(T) - 1] = f(10^3/T)$ characteristics and it was found to be $40\ meV$ at temperatures in the range $78 \div 140K$ and $0,25\ eV$ at $T > 150K$. For the band located at $1,66\ eV$, an activation energy of $0,29\ eV$ was found.

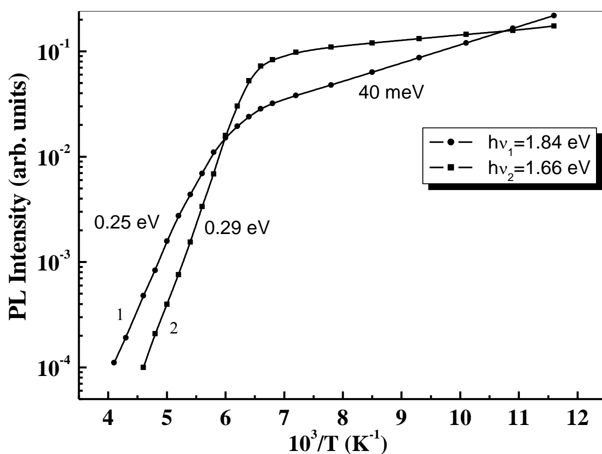

Fig. 7. Temperature dependence of photoluminescence intensity, L, for monocrystalline Ga_2S_3 layers.

Figure 8 illustrates the thermoluminescence (TSL) of monocrystalline Ga_2S_3 layers, after their excitation with light from the region by the vicinity of fundamental absorption edge, provided by a Hg lamp ($\lambda = 365\ nm$) and slow cooling to $78K$. TSL emission is determined by the presence of capture levels in the Ga_2S_3 crystal, from which, at temperature $78K$, electronic transitions normally do not occur. These electron capture states usually occur in crystals with native defects, where their concentration may be over $10^{19}\ cm^{-3}$ [4].

If one admits that the probability of repeated electron capture on the capture center is low, then TSL intensity is given by [5]

$$L(T) = \frac{\alpha\exp(-E/kT)}{\left[\frac{1}{n_0} + \frac{\alpha}{\beta}\int_{T_0}^{T}\exp(-E/kT)dT\right]^2} \tag{6}$$

where α is a constant depending on the compound nature, n_0 denotes the concentration of trapped electrons at starting temperature, T_0 (from which heating begins), and β is the heating rate of the sample. For α, β and n_0 constant in actual experimental conditions, the energy (E) of a certain capture level can be determined, in first approximation, by using the Urbach formula [22]

$$E = \frac{T_m}{A} \tag{7}$$

with $A = 500\ K^{-1}\cdot eV^{-1}$, and T_m-TSL glow peak temperature.

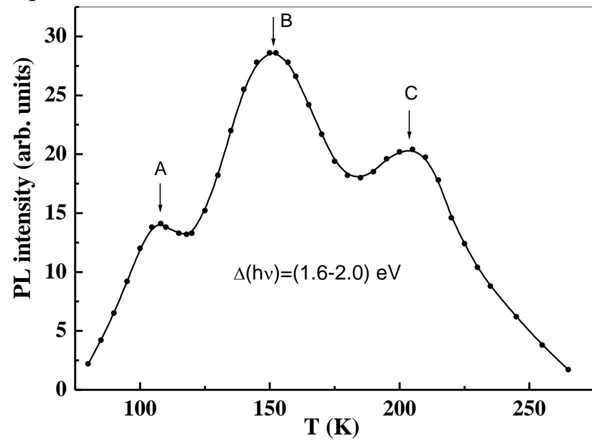

Fig. 8. TSL glow curve for monocrystalline Ga_2S_3 layers. PL excitation: Hg lamp (λ=365 nm). $\Delta(h\nu)$-spectral width of PL band.

As can be seen in Fig. 8, the $L(T)$ characteristics are composed of three bands, A, B, and C, with maximum at temperatures $108K$, $150K$ and $205K$, respectively. By using eq. (7), energies of electron capture levels in Ga_2S_3 monocrystalline layers have been calculated as $0,21\ eV$, $0,30\ eV$ and $0,41\ eV$, respectively. The value of $0,41\ eV$ agrees with that reported in [29], where respective acceptor level was found responsible for the green photoemission of $\alpha - Ga_2S_3$ crystals.

CONCLUSION

- Through the transport method in the vapors of I_2 were obtained $\beta - Ga_2S_3$ monocristals with hexagonal crystalline structure with lattice parameters $a = 11{,}15$ Å; $b = 6{,}36$ Å; $c = 7{,}06$ Å; and $\beta = 120^o56'$ characteristic to the $\beta - Ga_2S_3$ phase with small impurities of the $\alpha - Ga_2S_3$ phase.
- Fundamental absorption band edge of Ga_2S_3 at $T = 78K$ and $T = 293K$ crystals is determined by indirect optical transitions with optical photons emission. Indirect optical band width $(E_g^i - h\nu_f)$ equals to $(2{,}992_e + h\nu_f)$eV and $(3{,}07 + h\nu_f)$eV respectively at temperature of $293K$ and $78K$.
- At absorption coefficient $\alpha \geq 700\ cm^{-1}$ in $\beta - Ga_2S_3$ crystals are realized direct optical transition. Forbidden optical band width being equal to $3{,}149\ eV$ and $3{,}393\ eV$ respectively at temperature $293K$ and $78K$.
- In the PL spectrum of monocrystalline Ga_2S_3 layers excited above $2{,}50\ eV$, electronic transitions between the conduction band and the valence band tails participate. It is mainly composed of three photoluminescence bands, located at $2{,}04\ eV$, $1{,}84\ eV$ and $1{,}66\ eV$. The photoluminescence of Ga_2S_3 single crystals was found to obey first-order kinetics. The structural native defects engender deep recombination and capture levels for electrons within the Ga_2S_3 forbidden band. The energies of the capture levels in the monocrystalline layer were found as $0{,}21\ eV$, $0{,}30\ eV$ and $0{,}41\ eV$.

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