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Studies on Cu_2SnS_3 quantum dots for O-band wavelength detection

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In this communication, we report on Cu_2SnS_3 quantum dots synthesized by the solvothermal process using different solvents. The optical properties of the quantum dots are analyzed by UV-Vis-NIR and photoluminescence spectroscopy. The results suggest that Cu_2SnS_3 material has tunable energy bandgap and appropriate wavelength for fabrication of light emitting diodes and laser diodes as sources for fiber optic communication. They exhibit wide absorption in the near infrared range. Further morphological studies with the use of atomic force microscope confirm the surface topography and the existence of quantum dots. The observed characteristics prove the efficiency of Cu_2SnS_3 quantum dots for O-band wavelength detection used in fiber optic communication and solar cell applications.

Keywords: *solar cells; optical communication; Cu_2SnS_3; O-band wavelength*

1. Introduction

Nonlinear optical semiconductor quantum dots (QDs) are the building blocks of next generation photonics technology, due to their unique applications in fiber optic communication, ultrafast photonics, optical limiting and switching [1–3]. Semiconductor QDs are a special nanomaterial with unique tunable properties due to 3D confinement of electrons and holes. The 3D quantum confinement produces blue shift in the optical resonance with respect to QDs sizes; this is an important phenomenon, enabling us to produce the devices from the same constituents, which make the QDs operate at the same wavelength [4]. QDs are dominant in the strong confinement regime, so the QD laser diodes (QD LD's) are able to have an ultralow lasing threshold. The important aspect of 3D confinement keeps electron-hole pair well controlled so that the optical properties of QDs are independent of temperature. The advantages of temperature independence lead to developing high stability. Quantum dot devices, such as QD LD's and QD lasers, act as sources for fiber optic communication.

PbSe, PbS, PbS_xSe_{1-x}, CdS, CdSe, Cu(InGa)Se QDs are extensively investigated, popular QD materials. Researchers suggest that these are the best materials for optical applications and solar cells [5–7]. However, the toxicity level present in Pb and Cd is very high and moreover, the cost of indium and gallium is very high. This limits their usage for widespread applications. In this regard, we need some unconventional nanomaterials for making QD LD's. Thus, on a par with existing materials, some reports on copper tin sulfide QDs, such as Cu_3BiS_3, Cu_2ZnSnS_4, $Cu_2CoS_nS_4$, have already been reported by some researchers. Copper tin sulfide QDs is basically a p-type semiconductor for optoelectronic applications with the bandgap range of 0.93 eV to 1.77 eV. It has high absorption coefficient value of 1×10^4 cm^{-1} and its important advantages are nontoxicity, earth abundance; it is also cheaper than other materials [8]. The Cu–Sn–S based systems consist of different phases of components,

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such as Cu_2SnS_3, Cu_3SnS_4, Cu_4SnS_4, $Cu_2Sn_3S_7$, $Cu_5Sn_2S_7$, etc., amongst which Cu_2SnS_3 phase is the most often studied ternary semiconductor for optoelectronics applications such as fabrication of LD's and light emitting diodes (LED's) [9].

In fiber optic communication, a number of transmission bands are defined and standardized from O band to U-XL band as shown in Fig. 1 [10]. Based on the International Telecommunication Union, Telecommunication Standardization Sector [ITU-T], the wavelengths used for fiber optic communication corresponds to the wavelength bands related to the lowest transmission loss present in the optical fiber, as shown in Fig. 2 [11, 12]. Depending on the loss, the range is divided into six telecommunication operating wavelengths for fiber optic communication, namely O-band (original), E-band (extended), S-band (short), C-band (conventional), L-band (long), U/XL-band (ultralong). In the mentioned six bands, E-band and U/XL-band have higher transmission losses over other bands. U/XL is not used very often but further research is going on that wavelength [13].

Name	O	E	S	C	L	U/XL
Wavelength range(nm)	1260-1360	1360-1460	1460-1530	1530-1565	1565-1625	1625-1675
Observation	Original band	Water peak band		Bands used by the higher performance systems		Not used

Fig. 1. ITU-T based optical wavelength bands; the arrow represents wavelength increase and the general trend toward higher performance systems.

Among all these bands, O-band wavelength was used first in fiber optic communication because of small dispersion. But its bandwidth is highly limited to less than 10 km. Hence, it is not suitable for improving the bandwidth. Similarly, S-band also is not up to the mark to improve the bandwidth. The C-band seems to be the most appropriate for fiber optic communication due to low losses in transmission, which also facilitates good optical communication. At around 1400 nm and 1250 nm strong absorption of OH^- groups takes place. This leaves two windows for fiber optic communication: the region ranging from 1525 nm to 1565 nm and the region from 1360 nm to 1460 nm. These window regions are mostly used commercially for fiber optic communication [12, 14, 15].

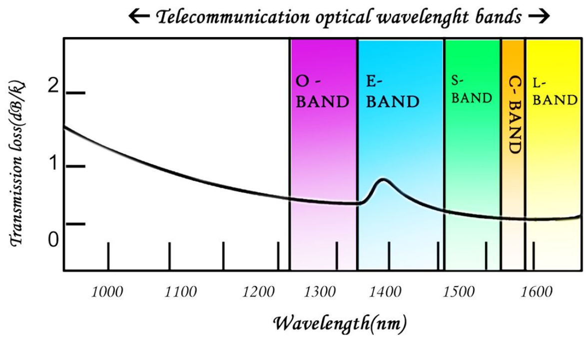


Fig. 2. Transmission loss in optical fiber in fiber optic communication wavelength bands.

Since operating at 1550 nm wavelength provides the best performance of glass fiber for long distance communication due to minimal loss, it seems logical to choose 1550 nm at every link, though the major part of the link cost depends on the applied laser. However, the laser operating at 1550 nm is very difficult to fabricate and the materials used for its fabrication are very costly. Furthermore, sophisticated instruments are needed for their investigation; moreover stability of these materials is still under researchable. Because of these drawbacks researchers prefer to work with a 1310 nm wavelength laser which is easy to fabricate. For short link communication within the range of 10 km, 1310 nm LD's or LED's would be typically used, it provides good performance at low cost. From the literature [8, 9, 26], it is suggested that Cu_2SnS_3 QDs have high stability and attain 1310 nm operating wavelength.

1.1. O- band wavelength possible application

Fiber optic communication networks have been developed for long distance communication, due to their low loss and high speed data transfer. The rapid progress in data services and telecommunication has led to increasing demand for capacity of all types of data transmission systems. The important features required for short data transmission systems which can be used in mobile backhaul systems or data storage are the reduced size and cost. The O-band (1310 nm) wavelength range is advantageous for medium and short range data transmission. The key aspects of 1310 nm wavelength range are the virtual lack of chromatic dispersion related to signal distortion and wide availability of components such as electro absorption modulators (EAMs) and semiconductor optical amplifiers (SOAs) [16].

SOAs and EAMs allow low transmission with nominal bit rates of 40 Gb/s to 50 Gb/s over the range of few dozen of kilometers at low cost and simple installation procedure. The most recent advancements in transmission strategies in the 1310 nm wavelength range have shown tremendous results up to 400 Gb/s DWDM (dense wavelength data multiplexing) concerning data transmission [17], an integrated 4 × 40 Gb/s transmitter assembly [18, 19], 50 Gb/s laser modulation [20], wavelength multiplexed 2 × 50 Gb/s multitone transmission [21] and 50 Gb/s laser and EAM integration [22]. There is a wide scope for O-band wavelength ranging from 1260 nm to 1360 nm; more specifically 1310 nm will meet good data transmission with increasing number of b/s in telecommunication applications.

2. Synthesis of quantum dots

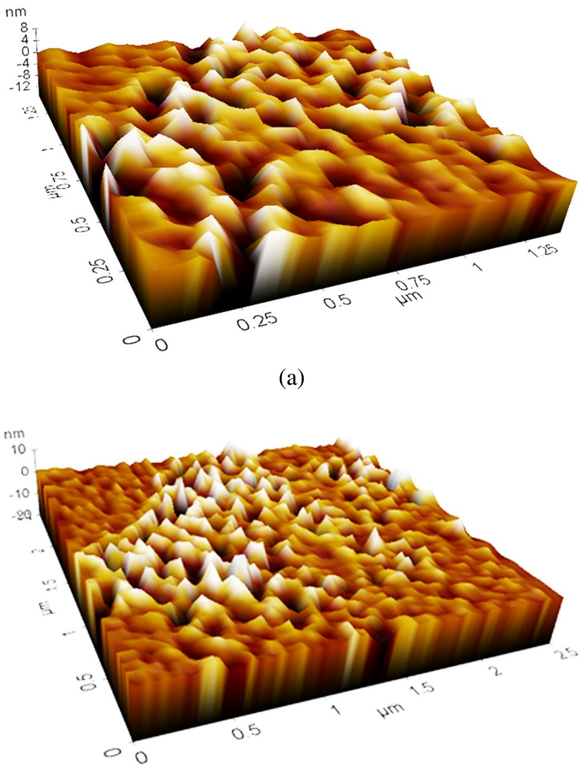
Cu_2SnS_3 QDs have been synthesized by using solvothermal method. It is a simple and effective method to produce QDs. 6 mmol of copper iodide, 3 mmol of tin (IV) acetate and 9 mmol of 1-dodecanethiol (DDT) were taken in a round bottomed three neck flask and the reaction mixture was degassed under vacuum for 6 min and for further removing of unwanted gas from the glass, argon gas was purged 4 times. Here, the DDT acted as a solvent and source for sulfur as well as the capping agent, hence, it controlled the growth and dimensions of the QDs so as no other extra precursors were needed in this process. Then, the flask was heated to 100 °C for 5 min and its temperature was increased further to 200 °C. During the process the color of the reaction mixture changed from light yellow to red and finally to black, which was followed by nucleation and growth of QDs. The samples in different colors were collected from the flask at different timings. Further, the QDs were separated and purified by using acetone followed by centrifugation and decanting.

3. Results and discussion

Atomic force microscope (AFM) in non-contact tapping mode was used to study the surface morphology of QDs obtained at different times and temperatures. Fig. 3a shows the AFM image of QDs obtained after 5 min at 100 °C. It is observed that QD growth has been initiated, the size of the QDs ranged from 1 nm to 4 nm. This was low temperature growth and hence, the energy band gap of the material was high, according to Brus equation. The temperature was further increased to 200 °C with 5 min interval. The AFM image in Fig. 3b clearly shows excellent growth of QDs with less energy band gap. The size of the QDs is between 5 nm and 10 nm, which is very suitable for fiber optic communication operating wavelength and solar cell applications.

Chemical state, electronic state and elemental composition of Cu_2SnS_3 QDs analyzed by XPS (X-ray photoelectron spectroscopy) have already been reported in the literature [23–29] and they seem to prove its material composition. From the literature [23–29], it is known that the core level spectrum of Cu 2p splits into $2p_{3/2}$ with a binding energy of 932 eV and $2p_{1/2}$ with a binding energy of 952.2 eV. Sn 3d splits into $2d_{5/2}$ with a binding energy of 486.7 eV and $2d_{3/2}$ with a binding energy of 495.1 eV. S splits into S $2p_{3/2}$ with a binding energy of 161.6 eV and S $2p_{1/2}$ with a binding energy of 162.4 eV. These results signify that valence states of Cu, Sn and S, in Cu_2SnS_3 QDs are in +1 oxidation state, +4 oxidation state and −2 oxidation state, respectively.

Fig. 4 shows the optical absorption spectrum of Cu_2SnS_3 QDs obtained in the wavelength range of 300 nm to 1400 nm. The energy bandgaps of this material, calculated using equation $E = hc/\lambda$, are 0.93 eV and 0.97 eV. When temperature increases, reaction time and the size of QDs also increase, whereas the energy bandgap decreases,



(a)

(b)

Fig. 3. AFM image of Cu_2SnS_3 QDs grown at 100 °C; (b) AFM image of Cu_2SnS_3 QDs grown at 200 °C.

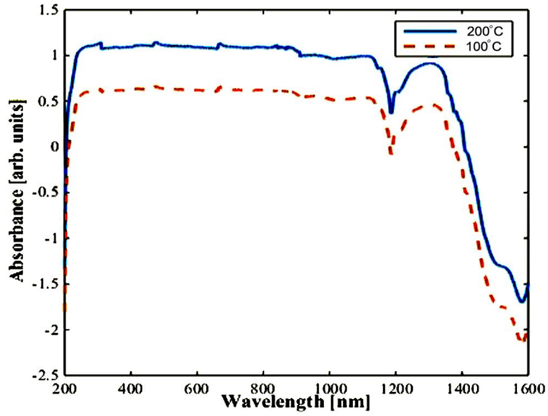


Fig. 4. UV-Vis-NIR spectra of Cu_2SnS_3 QDs.

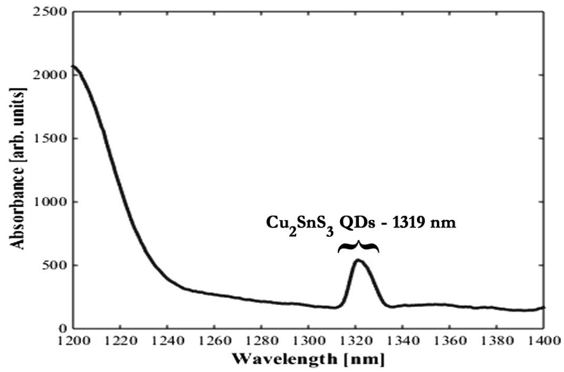


Fig. 5. Photoluminescence spectra of Cu_2SnS_3 QDs.

thereby confirming the quantum confinement effect in the QDs. The absorption spectra clearly reveal a significant red shift of optical absorption spectrum after complete growth of Cu_2SnS_3 QDs. Moreover, the strong optical absorption in infrared range (1300 nm) suggests that the material is a perfect candidate for infrared photodetector and solar cell applications.

Fig. 5 shows the photoluminescence spectra of Cu_2SnS_3 QDs. It is clearly seen that the peak is formed in the infrared range at 1319 nm, which is favorable for fabricating laser diodes and LED's for fiber optic communication sources. As mentioned before, the three ranges of operating wavelength commercially preferred to use, are 850 nm, 1310 nm and 1550 nm. Although for low distance communication, 850 nm and 1310 nm are preferred, but 1310 nm wavelength is the most commonly used operating wavelength for data transmission applications. Cu_2SnS_3 QDs can easily be tuned to achieve this wavelength so it is an appropriate material for fabricating LD's and LED's.

4. Conclusions

Cu_2SnS_3 QDs were prepared by solvothermal method with the use of different solvents. Optical properties and morphological structures were analyzed using UV-Vis and photoluminescence methods. From the observed results the following conclusions have been drawn. The Cu_2SnS_3 shows excellent optical absorption properties in visible and infrared regions with direct energy bandgaps of 0.93 eV and 0.97 eV and it emits infrared wavelength at 1319 nm. This is a favorable and practical operating wavelength for fiber optic communication. The work presents further research on Cu_2SnS_3 nontoxic material instead of other copper based material. The optical properties of Cu_2SnS_3 suggest that it is a promising material for fiber optic communication sources and future solar cell applications.

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