# Synthesis and Characterization of Silver Sulphide Quantum Dots by UV-AVA Spectroscopy

Ekpekpo Arthur and Chukwuka D. Doris

***Abstract*—This results of the experimental investigation of the synthesis and characterization of Silver Sulphide Quantum Dots is presented. In this work, silver quantum dots were synthesized using the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Different numbers of SILAR circles, ranging from four to ten circles of Silver Quantum Dots were synthesized. Tin II Chloride was used as the reducing agent which reduces silver hydroxide to silver. A colourless substrate immersed in the container of Tin II chloride solution before its immersion in the container of silver nitrate solution was observed to be brown which increases with the number of SILAR cycles as a result of the formation of silver quantum dots on it. The number of cycles directly determines the size of the quantum dots produced. Exposure of these substrates with silver quantum dots to hydrogen sulphide for 10minutes in a fume chamber using the Kipp's apparatus converted the silver quantum dots to silver sulphide quantum dots thereby making the substrates to become dark brown. The synthesized Quantum Dots were characterized using UV-SPEC2048 Spectroscopy machine. The absorption spectra exhibit a blue shift with decreasing size of silver sulphide quantum dots. This is due to the quantum size effect. The band gap of silver sulphide quantum dots with their respective sizes was calculated and it was found that the average band gap of the synthesized silver sulphide quantum dot is 1.80eV. This is higher than the band gap of bulk silver sulphide semiconductor which is about 0.9eV.**

***Index Terms*—Quantum dots, silver sulphide, nanoparticles.**

## I. Introduction

In recent years, metal chalcogenide semiconducting Quantum Dots have received much attention due to their world-wide applications in various fields of sciences and technology. [1].

The only well characterized solid compound of Silver and Sulphur is Silver (1) Sulphide ($Ag_2S$). It exists under ordinary pressure in three well defined crystalline modifications, usually designated X-, B-, and V- Silver Sulphide ($Ag_2S$), with X-Ag2S as the low temperature phase. [2].

Silver Sulphide is an important chalcogenide compound which has been investigated for its numerous applications. Semiconductor $Ag_2S$ belongs to II-VI compound semiconductor materials with monoclinic crystal structure. The semiconductor silver sulphide quantum dots have promising photoelectric and thermoelectric properties [3]. They can be used as

1) Infrared detectors [4]
2) Photoconductors and electrochemical storage cells
3) Silver is not a toxic metal unlike many other heavy metals hence Silver Sulphide quantum dot is good for application in the biomedical field.[5]

The use of Silver Sulphide quantum dots of comparable size would for instance enables one to image and treat cancerous cells simultaneously. This should drastically reduce the time and number of invasive procedures. Thereby increasing the efficiency of the treatment and most importantly the patient's quality of life.

The high absorbance in the UV region (<400nm) makes silver sulphide an important material in photovoltaic technology. [6]

## II. Materials and Method

In this work, the Successive Ionic Layer Adsorption and Reaction (SILAR) is selected to prepare Silver Sulphide quantum dots with the use of common and inexpensive chemicals as well as a basic characterization of the synthesized quantum dots. The substrates, microscope slides (25mm × 76.2mm × 1.2mm) were used to deposit nanocrystalline silver quantum dot by the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Before the deposition of the silver quantum dot on the substrates, a cleaning process was applied to the substrates. Initially they were put into a beaker containing distilled water and kept ten minutes to remove contaminants such as dust. Thereafter, they were brought out and dried. They were then degreased by chronic acids ($H_2SO_4$ and $HNO_3$) for some hours. Finally, they were rinsed with deionised water. A solution of ammoniaca silver nitrate was made by adding some drops of ammonia solution to Silver nitrate. This led to a colour change from dark brown to colourless. Some water was then added. Tin II Chloride solution was made by adding 5ml of HCL to 1g of Tin II Chloride to dissolve it. Thereafter 500ml of water was added. This constitutes the sensitizer solution. Tin II Chloride is a reducing agent. It reduces Silver hydroxide (AgOH) to Silver (Ag), it also helps the production of the silver quantum dots and controls their growth. It is worthy of note that the use of Tin II Chloride in the production and growth control of silver quantum dots is a special method used by the physics advanced laboratories, SHESTCO, Abuja. The etchant is made of 5ml HCl mixed with 250ml $H_2O$.This is used to etch the slide once per cycle after the third SILAR Cycle. The cationic precursor for the nanocrystalline silver sulphide quantum dots was ammoniaca Silver Nitrate while the source of Sulphur was hydrogen sulphide.

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The authors are with the Department of Physics, Delta State University, Abraka (e-mail: arthurekpekpo@yahoo.com).

To deposit Silver quantum dots, one SILAR cycle involves the following four steps

1) A well cleaned substrate is immersed in the first vessel containing the sensitizer which is Tin II Chloride solution.
2) The rinsing vessel containing distilled water where the substrate is rinsed for 30seconds
3) It is then taken to the container of Ammoniaca Silver Nitrate solution which is the cationic precursor. It stays in this container for one minute.
4) The rinsing container where it is rinsed again for 30seconds thereby completes the first SILAR cycle.

Repeating these processes, a thin film of Silver quantum dots was deposited on the substrate. The thickness of the deposited film depends on the number of SILAR cycles. It must be noted that substrate was etch and rinse each cycle after the third SILAR cycle. These substrates with different layers of Silver quantum dots were Sulphurized by passing hydrogen sulphide gas through them in a conical flask using the Kipp's apparatus in a fume chamber.

## III. Synthesis Techniques

In this work, Silver Sulphide ($Ag_2S$) quantum dots were synthesized by using the SILAR technique. Silver (Ag) quantum dots was synthesized first, thereafter the samples were sulphurized using the Kipp's apparatus in a fume chamber.

The SILAR technique is used for the following reasons, it is simple, fast, cheap and harmless.

The images below shows some samples of silver (Ag) quantum dots using the method described by [7] (see Plate 1 - Plate 3).

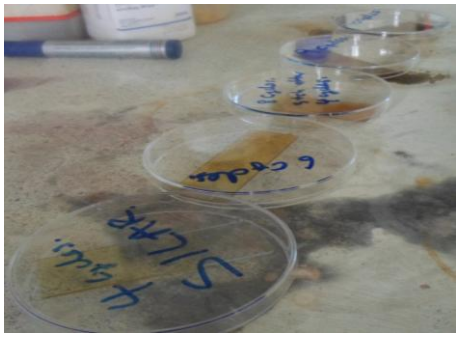

Plate 1. Samples of silver (Ag) quantum dots.

Plate 2. Sulpurization of the synthesized silver (Ag) quantum dots.

## IV. Characterization

The synthesized silver sulphide ($Ag_2S$) quantum dots were characterized in the physics advanced laboratories, SHESTCO, Abuja using UV-Spec 2048 spectroscopy machine. The absorbance of the samples was measured by this dual beam spectrometer with respect to a reference sample which is slicon wafer.

Plate 3. Dual beam spectrometer of UV-spectroscopy.

## V. Results and Discussion

Some samples of silver quantum dots were synthesized by the SILAR techniques. Thereafter, they were sulpurized by passing hydrogen sulphide gas through them using the kipp's apparatus. These samples were sulphurized to get silver sulphide quantum dots ($Ag_2S$). They were all characterized but two out of these samples were contaminated as indicated by their absorbance spectra. There was non-uniformity and presence of noise in their absorbance amplitude.

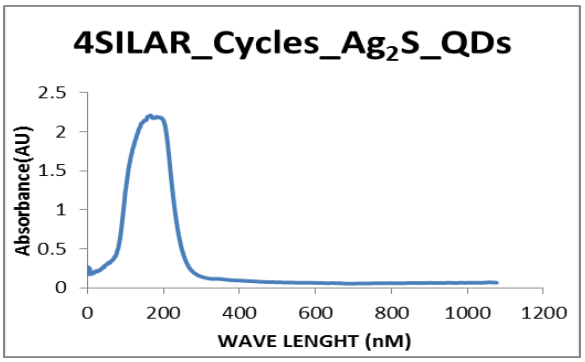


Fig. 1. UV Absorption spectra for 4 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

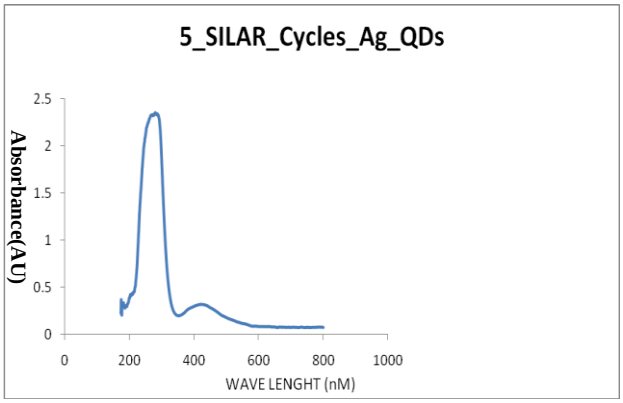


Fig. 2. UV absorption spectra for 5 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

The uncontaminated samples were further investigated so that the wave length corresponding to each absorbance peak was extrapolated and substituted into the formula

$$E_g = \frac{hc}{\lambda} \quad (1)$$

Also the diameter (d in nm) of the synthesized quantum dots was calculated using the empirical formula.

$$Eg = 0.41 + (0.0252d^2 + 0.283d)^{-1} \quad (2)$$

The UV-spectra of synthesized silver sulphide ($Ag_2S$) quantum dots are presented below

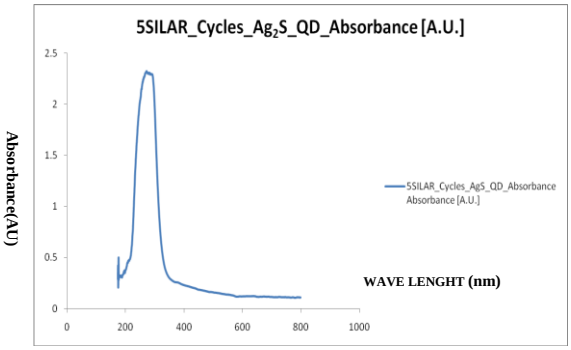


Fig. 3. UV absorption spectra for 6 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

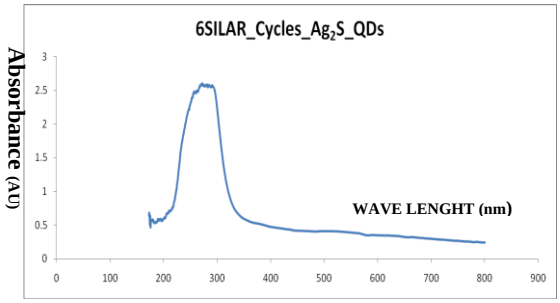


Fig. 4. UV absorption spectra for 7 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

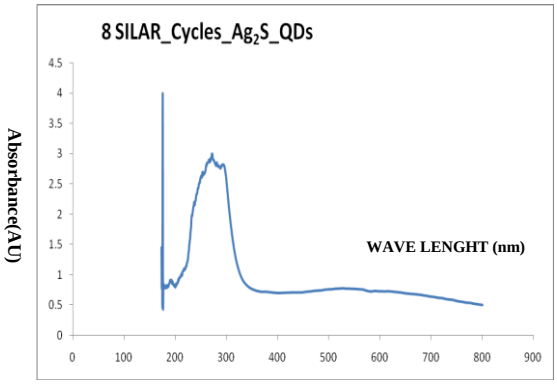


Fig. 5. UV Absorption spectra for 8 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

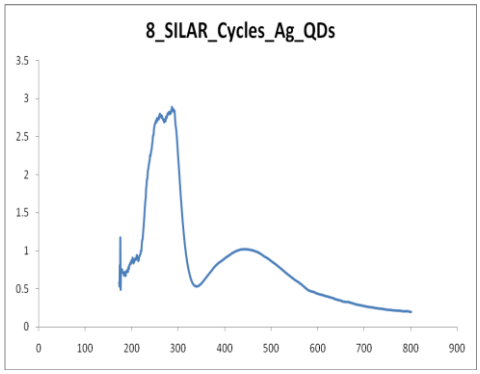


Fig. 6. UV absorption spectra for 9 SILAR cycles of $Ag_2S$ quantum dots with absorbance peak and wavelength.

The results show highest absorbance in the UV-region ( < 400nm). The optical band gap energy was found to be 1.8ev.

TABLE I: EXTRAPOLATED WAVELENGTH OF EACH QUANTUM DOTS AT VARIOUS ABSORBANCE PEAK

| Name of Nano particles | Wavelength at absorbance peak (nm) |
|---|---|
| 4 SILAR $Ag_2S$ | 370 |
| 5 SILAR $Ag_2S$ | 375 |
| 6 SILAR $Ag_2S$ | 381 |
| 7 SILAR $Ag_2S$ | 385 |
| 8 SILAR $Ag_2S$ | 395 |
| 9 SILAR $Ag_2S$ | 400 |

Using the De Broglie relationship, $E_g = \frac{h_c}{\lambda}$

where $E_g$ is the band gap of the nanoparticle. C is the speed of light in space ($3 \times 10^8$m/s) and $\lambda$ is the wavelength at each absorbance peak. The band gap of each nanoparticle as a function of wavelength was calculated. This is shown in the Table I and Table II below:

TABLE II: CALCULATED BAND-GAP

| Name of Nano particles | $\lambda$ (nm) | Band Gap(eV) |
|---|---|---|
| 4 SILAR $Ag_2S$ | 370 | 1.41 |
| 5 SILAR $Ag_2S$ | 375 | 1.38 |
| 6 SILAR $Ag_2S$ | 381 | 1.34 |
| 7 SILAR $Ag_2S$ | 385 | 1.32 |
| 8 SILAR $Ag_2S$ | 395 | 1.29 |
| 9 SILAR $Ag_2S$ | 400 | 1.28 |

Concurrently, the nanoparticle diameter (size) was calculated using the relation.

$$R = \sqrt{\frac{2\pi^2 h^2 E_g^{\ b}}{\left(\frac{1}{M^*_e} + \frac{1}{M^*_e}\right)\left(E_g^{\ n^2} - E_g^{\ b^2}\right)M_o}} \quad (3)$$

where:

$R$ = quantum dot radius

(2 $R$ is the diameter and hence, indicates particle size)

$E_g^b =$ bulk band gap for Cds and CdSe

$E_g^n =$ the band gap calculated from the excitonic absorption wavelength of $Ag_2S$ in table 4.2 above.

$M_e^* =$ the effective mass of the electron.

$E_g^b =$ the effective mass of hole, in kg.

TABLE III: CALCULATED BAND-GAP AND QUANTUM DOTS DIAMETER FOR AG2S

| Name of Nano particles | $\lambda$ (nm) | Band Gap (eV) | Diameter (nm) |
|---|---|---|---|
| 4 SILAR $Ag_2S$ | 370 | 1.41 | 2.7 |
| 5 SILAR $Ag_2S$ | 375 | 1.38 | 2.9 |
| 6 SILAR $Ag_2S$ | 381 | 1.34 | 3.0 |
| 7 SILAR $Ag_2S$ | 385 | 1.32 | 3.1 |
| 8 SILAR $Ag_2S$ | 395 | 1.29 | 3.3 |
| 9 SILAR $Ag_2S$ | 400 | 1.28 | 3.5 |

From the result of Table III, a graph of band gap was plotted against the diameter of the quantum dot. This is shown in the figure below

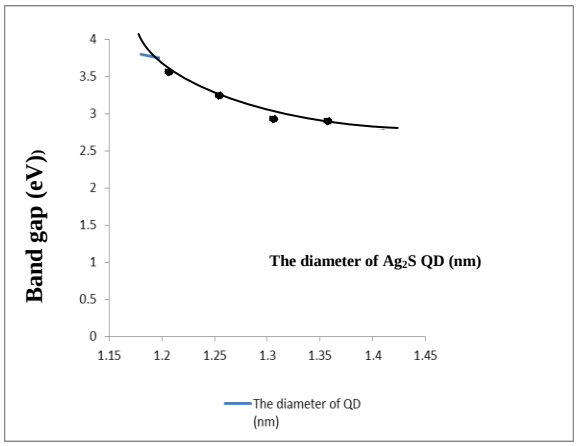


Fig. 7. A graph of band gap versus the diameter of $Ag_2S$ QDs.

## VI. Discussion of the UV-Spectral

The UV-Spectral presented in the above Fig. 1 - Fig. 7 show that as the size of the quantum dot decreases, the absorbance peak shifted to a shorter wavelength. This leads to an increase in the confinement energy because the valence band is move downward while the conduction band is move upward. Thereby increasing the energy band gap of the quantum dot. This is why the band gap of the synthesized Silver sulphide quantum dot was greater than the band gap of the bulk silver sulphide material. In a bulk semiconductor, the conduction electrons are free to move around in the solid ,so their energy spectrum is almost continuous, and the density of allowed electron states per unit energy increases. Therefore, if one can synthesize a piece of semiconductor so small that the electrons feel confined, then the continuous spectrum will become discrete and the energy gap will increase.

The control of the size allows us to engineer the optical properties of a semiconductor with strong absorption occurring at certain photon energies. This qualitative picture of the effects of quantum confinement in semiconductors is supported by [8].

The obvious optical feature of the synthesized quantum dots is in their colour. Though these quantum dots were made of the same materials, yet the substrate with the largest quantum dots (10SILAR cycles)

Was the most dark while the substrate with the smallest quantum dot (4SILAR cycles) was the least dark sample. The colouration is directly related to the energy levels of the quantum dot. Quantitatively, the band gap energy determine the energy (and hence the colour) of the fluorescence light which is inversely proportional to the size of the quantum dot. [9]. The increase surface area/volume ratio and the accompanied increase in oscillator strength as a result of the downsizing of the bulk silver sulphide to the nanoscale range is responsible for the increase in the band gap of the synthesized quantum dots compare to their bulk counterpart. [10].

## VII. Conclusion

The absorption spectra features maximum peak with corresponding wavelength which increases with the number of SILAR cycles. It shows a uniform distribution of particles, where the grains are small. The dots were found to have high absorbance in the ultra violet region and depreciate as the wavelength increased. They have high transmittance in the visible near infra-red region. The energy gap for the fabricated $Ag_2S$ Quantum Dots was found to be 1.80eV and it was also found that the bond gap increases by decreasing the size of the Quantum Dot due to the increase in the quantum confinement effect. Many features of Silver Sulphide Quantum Dots are relevant to application in optoelectronic, telecommunications and biophysics.

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**Ekpekpo Arthur** is a member of IACSIT. He was born in Okuama, Ewu Clan on the 20th September, 1969. He obtained his B.Sc (Hons) in physics in Edo State University, Ekpoma, Nigeria (1989-1994), M.Sc. geophysics in Ambrose Alli University, Ekpoma, Nigeria (1997-1999), and Ph.D. solid state physics in Ambrose Alli University, Ekpoma, Nigeria (1999-2009). His major field is solid state physics.

He was a physics teacher at Federal Technical College, Zuru, Kebbi State of Nigeria (1994-1985). And he is a lecturer in the Department of Physics, Delta State University, Abraka.

He is currently the associate professor of solid state physics and the head of the Department of Physics, Delta State University, Abraka, Nigeria. Dr. Arthur is a member of Nigerian Institute of Physics, member of Nigeria Association of Mathematical Physics and a member of Science Association of Nigeria (SAN).

He published many articles and received many awards, such as Best 200-Level student, Best 300-Level student, Best graduating student etc..