Optical Properties and Band Offsets of CuS/ZnS Supperlattice.

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ABSTRACT

CuS/ZnS superlattice was deposited on glass substrates at room temperature using Successive Ionic Layer Adsorption and Reaction (SILAR) technique. X-ray diffractometer method was used to obtain structural characterization. A Janway 6405 UV/VIS spectrophotometer was used to obtain the optical spectral, optical absorbance, transmittance, extinction coefficient, and refractive index. A valence band offset of 0.55eV and conduction band offset of 1.05eV at CuS/ZnS interface were determined by optical method. The band alignment was found to be type 1. The energy band gaps of the ZnS, CuS, and CuS/ZnS are 3.75eV, 2.15eV, and 2.70eV, respectively, and refractive indices of 2.11 for ZnS films, 2.44 for CuS films and 2.31 for CuS/ZnS superlattice. The films showed a maximum transmittance of about 80% in NIR region and peak transmittance of 75% in the VIS region. The transmittance in the UV region was rather low.

(Keywords: semiconductor superlattice, SLS, band offset SILAR, successive ionic layer adsorption and reaction, optical properties)

INTRODUCTION

Semiconductor superlattices (SLS) were proposed about 40 years ago (Esaki et al., 1970). They are synthetic crystals which consist of either a periodic sequence of ultrahigh layers of two different semiconductors or a single homogenous semiconductor, which is periodically n-doped and p-doped. The semiconductor superlattice consists of periodic arrangement of two semiconductors of different energy band gaps (Smith, 1990). They are interesting model system for electrons in a periodic potential (Zhores, 2001).

The difference in their energy gaps leads to discontinuities in both conduction and valence bands, labeled as E_C and E_V, respectively, and a set of square wells separated by potential barriers forms. The existence of the superlattice potential was found to alter the energy spectrum, as a result of this, the superlattice have a number of fascinating characteristics and properties which non-superlalattice semiconductors do not have. It is found that an extremely wide spectrum of possibilities results from the fact that the properties of superlattice can be tailored for a given goal.

The superlattices really exist as a flexible material. The flexibility introduced by this design possibility makes superlattices useful in several technological applications, including semiconductor diode lasers (Holonyak et al., 1980), electro-optical modulators (Miller et al., 1985), nonlinear optical materials (Shang, 1985), infrared detector (Osbourn, 1984) and multilayer applications in p-i-n solar cells (Kuwano et al., 1987).

In this work CuS/ZnS superlattice was grown on glass substrates. As an important semiconductor with unique electronic, optical and chemical properties, CuS is a promising material with potential applications in many fields. This film has recently received considerable attentions, due to numerous technological applications in achievement of solar cells (Sukarova et al., 1997), in photo thermal conversion of solar energy (Nair et al., 1991) and as selective radiation filter on architectural windows (Nair et al., 1991).

The optical study shows that CuS has direct band gap of 2.36eV (Satale et al., 2000). These films have been prepared by the Successive Ionic Layer Adsorption and Reaction (SILAR). This SILAR method is an aqueous solution method based on sequential reactions at substrate-solution interface for the deposition of the thin films. It involves the alternate dipping of the substrates into aqueous solution containing ions of each component. In the SILAR technique,

quality films are obtained by optimizing some parameters such as concentration, temperature and pH of the precursor solutions and the time duration for adsorption, reaction and rinsing (Yildrim et al., 2009).

ZnS is an important material with an energy band gap E_g = 3.65eV (bulk), which has the largest value of the entire II-IV compound semiconductor. ZnS thin film is an n-type semiconductor characterized with a wide direct band gap. Therefore, it could be useful for the fabrication of n-window layers of solar cells, opto-electronic devices such as the blue light emitting diodes, electro-optical modulator and Mn-doped electroluminescent devices. Thus depositing CuS films on ZnS substrates form a promising material which is very useful in various science and technological applications. ZnS thin films have been grown on various substrates like silicon, glass, ITO and GaAs (Yan et al, 2007).

The annealing temperature effect on optical band gap and electrical properties of ZnS thin films has been reported and it was found that the optical band gap decreased with increasing annealing temperature, therefore, the annealed films was found to be more resistant than the as-grown films (Yildrim et al, 2009).

MATERIALS AND METHOD

In this study, CuS/ZnS superlattice was grown on glass substrates by the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. ZnS thin film was first grown on glass substrates and CuS thin films were deposited on ZnS substrates. For the preparation of the superlattice, the glass substrates were first cleaned in purified water, and dried in air. The glass substrates were immersed into a solution containing 0.1mol zinc chloride solution (pH 5) for 30s. The substrates were rinsed with distilled water for 40s to remove superfluous Zn^{2+} ions that interact rather weakly with the substrates. The substrates were then immersed into 0.05mol sodium sulphide solution (pH 12) for 30s and rinsed with distilled water for 40s. The substrates were dried in desiccators. These lead to the deposition of ZnS thin films on glass substrates. The above deposition cycles were repeated 100 times to get the desired film thickness. CuS thin films were deposited on ZnS substrates by immersed the substrates into copper chloride solution (pH 5) for 30s, rinsed with distilled water for 40s, moved to vessel

containing sodium sulphide solution (pH 12) for 30s and finally rinsed with distilled water for 40s.

These cycles were repeated 100 times to obtain the desired film thickness. The above process making up to 200 cycles lead to the fabrication of CuS/ZnS superlattice. The substrates were cleaned in acetone and stored in desiccators for drying. The thickness was measured using gravimetric method. The optical absorption spectra were measured using a Janway 6405 UV/VIS spectrophotometer. The structural measurements were done using X-ray diffraction techniques.

RESULT AND DISCUSSION

The Thickness of CuS/ZnS superlattice with 200 cycles on glass substrate was 5.45nm. It can be concluded that the average growth rate of CuS/ZnS films were 0.027nm/cycle. During the deposition processes, it was observed that the Cu^{2+} ions do not interact favorably with bare glass substrate. The adhesion of copper thin films on glass substrate was poor. This observation is in agreement with Lindroos et al., 2004. The zinc sulphide films interact very well with glass substrates. It forms good adhesion with the glass substrate. The absorbance spectra of the films were measured as a function of incident photon wavelength. A blank substrate was placed on the reference beam for all measurement to correct the absorption of the substrate. The energy band gap of the thin film samples were calculated with the help of the $(\alpha h\upsilon)$ ^{2} versus energy band gap values using the equation below:

$$\alpha\,(h\upsilon) = A(h\upsilon - E_g)^{1/2} \qquad\qquad \textbf{(1)}$$

where A is a constant and E_g is the the optical band gap. Thus, a plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is a curve line whose intercept on the energy axis gives the energy gap. The band gap energy of the film have been determined by the extrapolation of the linear regions on the energy axis, $h\upsilon$.

The absorption coefficient (α) associated with the strong absoprtion region of the film was calculated from absorbance (A) and the film thickness (t) using the relation:

$$\alpha = 2.303A/t \qquad\qquad \textbf{(2)}$$

The extinction coefficient (k) is evaluated from the relation:

K=αλ/4πt **(3)**

where λ is the wavelength of the incident radiation and t is the thickness of the film.

The optical energy gap of the pure CuS thin films deposited via this technique is 2.15eV and that of ZnS thin film is 3.75eV. The effect of putting some CuS in ZnS matrix drove the band edge to 2.70eV. The substrate absorption was corrected by introducing an uncoated cleaned glass in the reference beam. The refractive index was determined using Moss rule:

$n^4E_g = 77$ **(4)**

n=refractive index and E_g is the energy band gap. The refractive indices of ZnS film, CuS film, and CuS/ZnS superlattice were evaluated to be 2.11, 2.44 and 2.31, respectively. The optical transmittance spectra of the CuS/ZnS superlattice as a function of wavelength is shown in Figure 4.

The maximum transmittance in the visible region occurs at about 700nm. In the NIR region, a maximum transmittance of about 80% occurs at wavelength of 900nm. The high rate transmittance of the films in the NIR regions could be exploited in the glazing applications for space heating. The films show low transmittance and high absorbance in UV regions. The films could therefore act as UV filters on architectural windows. The thin films provide ultimate protection from UV radiation. The UV control is important and useful for the protection of both people and goods, since UV radiation is one of the main causes of fading and dermatological damage.

The transmittance in the visible region is 20%-75%. This high transmittance makes this material useful as a buffer layer of CIGS solar cell (Ezenwa et al., 2011).The optical studies of the films showed a very high absorbance in the UV regions and low absorbance in the NIR region.

Figure 5 is a plot of absorbance versus wavelength of the material. The absorbance decreases as wavelength increases. It has absorbance range of 0.008-0.089 at the wavelength range of (300-900) nm in the VIS region where it absorbs only slightly. This makes the material to be invaluable in effective windscreens coating and driving mirrors to prevent the effect of the dazzling light into driver eye.

The high refractive index makes the film to be very useful for poultry production, solar cells and anti-dazzling coating (Ezenwa et al., 2011). The optical studies of the films show very high absorbance in the UV region but falls off in the visible region. It showed low absorbance in the NIR region.

Figure 6 is a plot of extinction coefficient against the wavelength of CuS/ZnS superlattice. A peak extinc,tion coefficient value of 0.079 is obtained at wavelength of 900nm. The extinction coefficient increases continuously with increasing wavelength indicating high transmittance and low absorption in the NIR region. This also indicates high degree of absorption in the UV region.
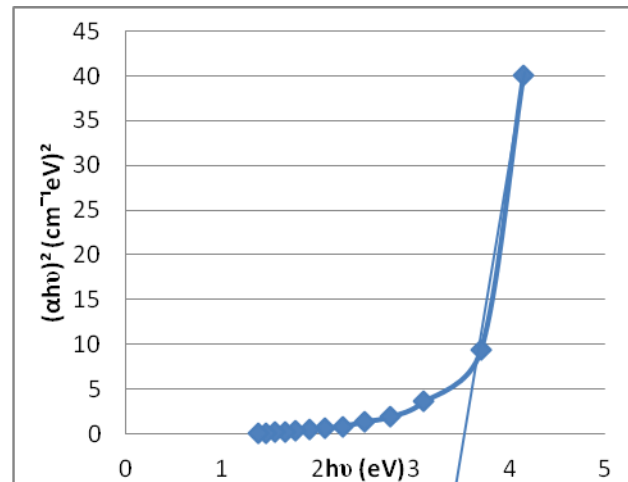

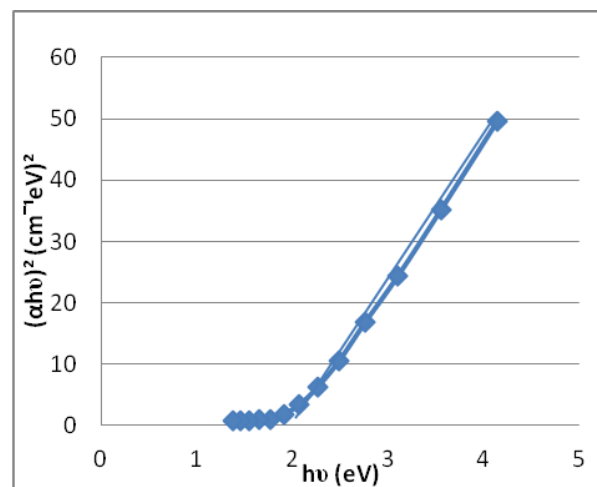**Figure 1:** The Optical Absorption Spectrum of ZnS Films.

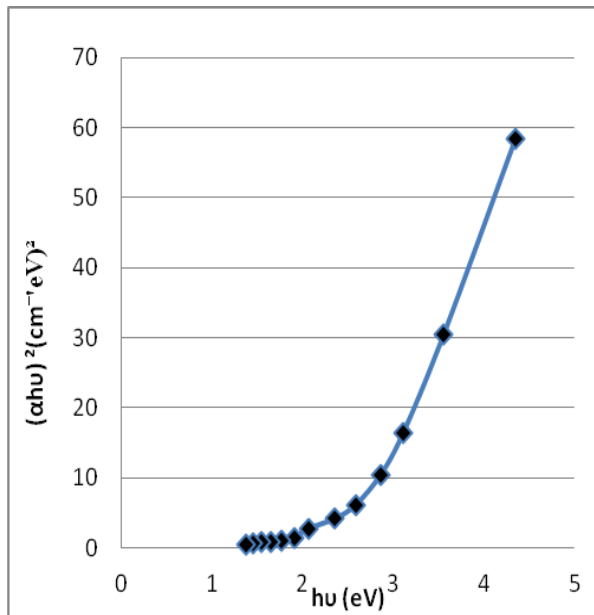**Figure 2:** The Transmittance Spectrum of CuS Thin Films.

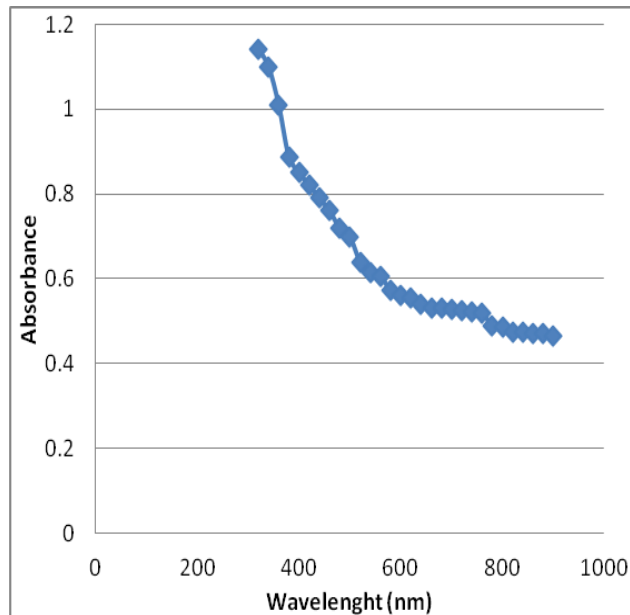**Figure 3:** The Optical Absorption Spectrum of CuS/ZnS Superlattice.

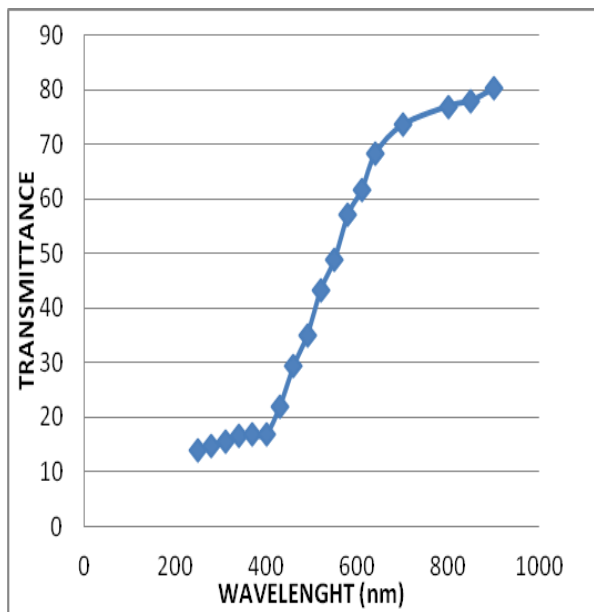**Figure 5:** The Absorbance Spectrum of CuS/ZnS Superlattice.

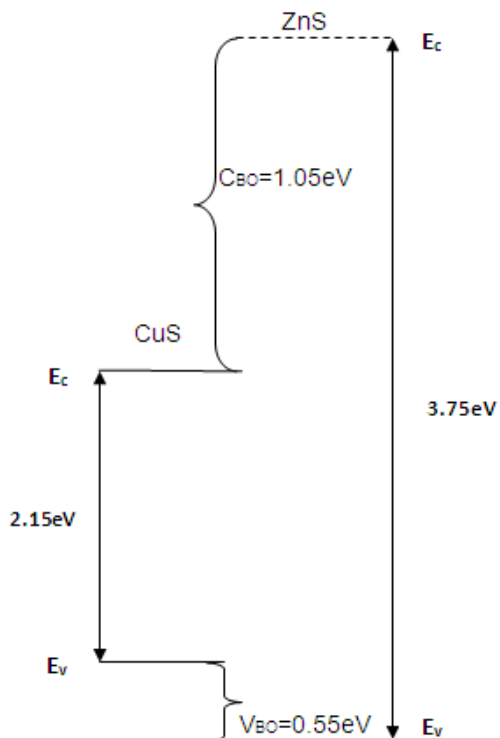**Figure 2:** The Optical Absorption Spectrum of CuS Thin Films.

Figure 6: The Band Alignments of CuS/ZnS.
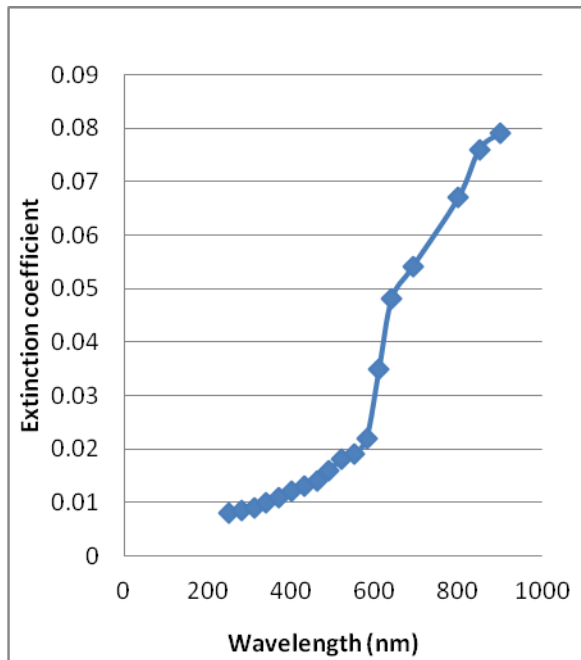
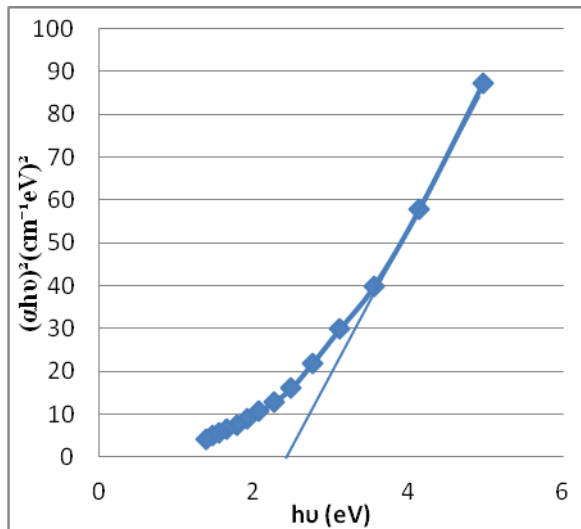**Figure 7:** The CuS/ZnS Extinction Coefficient Spectrum.

Figure 8: The Optical Absorption Spectrum of ZnS/CuS Superlattice.

Due to the high optical transmission of CuS/ZnS films, it can play an important role in photovoltaic solar cell devices. ZnS films are very suitable as a window layer in the heterojunction photovoltaic solar cells, because the wide band gap will decrease the window absorption losses and improve the short circuit current of the solar cell.

The value of the band gap of the chemically deposited ZnS in this work is in close agreement with those obtained by Nadeem and Ahmed (2000) and Ndukwe (1996). The ZnS films have been found invaluable in various devices such as antireflection coating for solar cell (Bloss et al., 1988), environmental friendly buffer layer as compared to CdS layer in CIS based thin film solar cell (Kashani, 1996), wide band gap materials for electroluminescent and Opto - electronic devices (Thewlis, 1979), as α – particle detector (Kashani 1996), photosynthetic coatings (Ndukwe 1996) and blue light emitting laser diodes (Hass et al, 1982).

The optical energy band gap obtained for CuS compares favorably with 2.2eV obtained by Nascus et al., 1997, 2.11eV by Mudi et al., 2009 and 2.03eV by Yildrim et al., 2009. The CuS has received numerous attentions due to various technological applications. It is useful as a selective radiation filters on architectural window (Nair et al., 1991), in photothermal conversion of solar energy (Nair et al., 1991), in achievement of solar cells (Sukarova et al., 1997), electro conductive electrodes, microwave shielding coatings, solar control coatings, potential nanometer-scale switch, cathode materials in lithium rechargeable batteries, and some chemical sensing application (Mudi et al., 2009).

CuS/ZnS superlattice consists of periodic arrangement of ZnS and CuS semiconductor respectively with different energy band gaps. The difference in their energy gaps leads to discontinuities in both the conduction and valence band and a set of square wells separated by potential barriers forms. The existence of the superlattice alters the energy spectrum. CuS/ZnS superlattice offers a unique possibility for altering their band structure practically arbitrary.

Figure 6 shows the schematic diagram for band alignment of CuS/ZnS superlattice. A valence band offset (V_{BO}) of 0.55eV and conduction band offset (C_{BO}) of 1.05eV were obtained.

Our C_{BO} value compares favorably with 1.1eV reported by Ricolleau et al., 1998. The band alignment of CuS/ZnS superlattice was found to be type 1, which compares favorably with results obtained by Ezenwa et al., 2011 and Kaur et al., 1980.
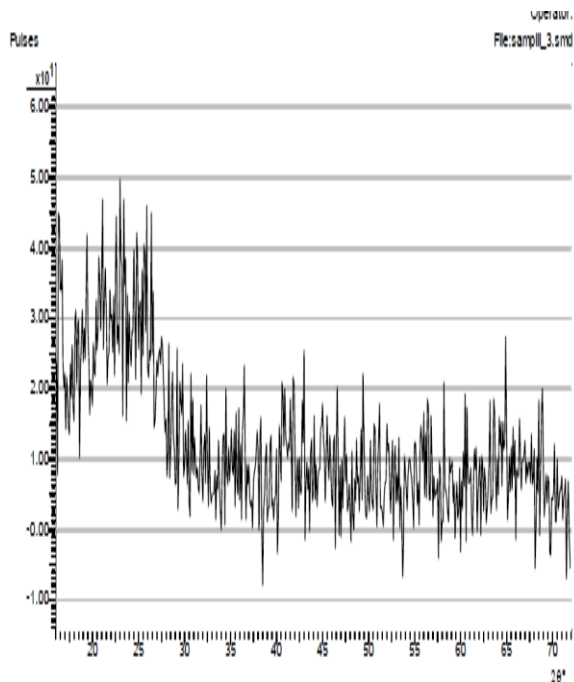
Figure 9: X-ray Diffraction Pattern of CuS/ZnS Superlattice.

Figures 1, 2, 3, and 8 show the optical absorption spectra of $(\alpha h\upsilon)^2$ as a function of photon energy $h\upsilon$ for ZnS film, CuS film, CuS/ZnS and ZnS/CuS superlattice, respectively. From the plots, the optical band gap energy of ZnS semiconductor, CuS semiconductor, CuS/ZnS and ZnS/CuS superlattices were obtained The values were found to be 3.75eV for ZnS, 2.15eV for CuS, 2.70eV for CuS/ZnS, and 2.60eV for ZnS/CuS.

The optical energy gap of the pure CuS thin films deposited via this technique is 2.15eV and that of ZnS thin film is 3.75eV. The effect of putting some CuS in ZnS matrix drove the band edge to 2.70eV for CuS/ZnS superlattice and 2.60eV for ZnS/CuS superlattice. The wide band gap makes the semiconductor materials suitable for photocell.

Figure 9 show the x-ray diffraction spectrum of CuS/ZnS. According to what is obtained from x-ray measurement, it actually indicates crystallization of CuS and ZnS in the cubic and hexagonal phases, respectively. This compares favorably with those obtained by Ezenwa et al., 2011 and Tsukasa et al., 2000. Many diffraction peaks of different intensity were obtained from the XRD spectra. The highest diffraction peak was noted at diffraction angle 23.50^{o} corresponds to (100) preferred orientation. The preferential

orientation of the films is along the (100) direction. However, the XRD spectrum of the CuS/ZnS layer deposited by chemical method only exhibit the (100) direction. The grain size of the film was calculated from XRD pattern using Debye Scherer's formulae:

$$D = 0.9\lambda \, / \, \beta cos\theta \qquad\qquad (5)$$

where D is the grain size, λ is the X-ray wavelength, β is the full wave at half maximum and θ is the Braggs angle. The crystallite size is 28.1 nm and the inter-planar spacing is 3.722 nm.

CONCLUSION

Successive Ionic Layer Adsorption and Reaction (SILAR) technique has been used to demonstrate the synthesis of CuS/ZnS superlattice. A band offset of 0.55eV was calculated at the CuS/ZnS interface, extinction coefficient of approximately 0.079 at 900nm and refractive index of approximately 2.39 at 2.70eV were obtained for CuS/ZnS superlattice.

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