Semiconductor quantum dots as nanoelectronic circuit components

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ABSTRACT
In this paper, a systematic investigation of frequency response of CdS and CdS:Cu quantum dot devices, following microwave-assisted synthesis, is presented. Phase of the output relative to the input as a function of frequency is also recorded to have some insight into the observed low-pass filter characteristics of the as-fabricated devices. The as-fabricated quantum dot devices are found to have all the characteristics of a classical low-pass filter with optimization of gain, phase shift and cut-off frequency in the band-gap range of '2.5–2.6' eV. The as-fabricated devices are tested for demodulation and satisfactory operation is obtained. This suggests for employing such nanoscale devices in the field of communications.

1. Introduction
Semiconductor nanocrystals have been investigated widely during recent years due to their potential applications in various fields of science and technology. The development in the field of quantum electronics encompasses revolutionary transition from vacuum tubes to transistors and then to integrated circuits. These features find their attractive presentation in the form of Moore’s law.[1] The on-going transition from microelectronics to nanoelectronics has further concretised the basic concept of the law.

The necessity for transition from microelectronics to nanoelectronics/nano-optoelectronics calls for proper understanding of the physics of the nanoscale devices. The circuit elements, e.g. resistors (R), inductors (L) and capacitors (C) which are the basic building blocks of microelectronic devices for information processing, storage and communications, need to be scaled down to the terahertz, infrared and visible wavelength regions in order to obtain high density, high speed analogues of the traditional circuits. Experimental verifications of nanofilters in the 8–14 μm wavelength domain have been demonstrated by Sun et al. [2] in 2010. Caglayan et al. in 2013 [3] presented the first designable near-infrared (NIR) lumped nanocircuits with tailorable response. Very recently, Maaza et al. [4] has reported the first-order semiconductor metal Mott transition in single nanocrystal of VO₂ using scanning tunnelling spectroscopy. This important contribution has paved
the way for engineering reversible and tunable VO₂ nano-scaled femtosecond optoelectronic gates.

The physics of the nanoscale devices with emphasis on application is an intersection of quantum mechanics and the classical electronic circuit theory. Of the various building blocks of nanoscale devices, quantum dots are the most significant ones as the complete quantum confinement of charge carriers is achieved in them, which gives rise to the possibility of having full quantum effects in these structures. Wang et al. [5] on the basis of their theoretical investigations found that a quantum capacitor consisting of a quantum dot and a large metal conductor is equivalent to a classical resistor-inductor-capacitor (RLC) circuit with three basic parameters: a static electrochemical capacitance $C_m$, a charge relaxation resistance $R_q$ and a quantum inductance $L_q$. They obtained $L_q \sim R_q \tau$, where $\tau$ is the characteristic time scale for the quantum dot such as the dwell time $\tau_d$ or the tunnelling time $\tau_t$. Due to the phase delay by the quantum inductance, the dynamic current can lag behind the applied ac voltage, giving rise to a negative capacitance. Their numerical results show that this effect should be detectable experimentally using the present device technology. Fu et al.,[6] inspired by the experimental findings of Brown et al. [7] and of Gering et al. [8], put forward a theoretical model for a Resonant Tunnelling Diode (RTD) deriving Landauer-Buttiker formula for ac transport. They found that for such device admittance is capacitive at low frequencies and inductive at higher frequencies.

Begliarbekov et al. [9] investigated theoretically high-frequency ac transport through graphene nanoribbons with top gate potentials that form a localised quantum dot. They showed that above a sufficiently high frequency, the behaviour of the graphene nanoribbon device is analogous to a classical RLC oscillator. These results indicate that coupling of the inductive behaviour of a quantum dot to the gate tunable quantum capacitance in graphene gives rise to an in situ tunable ultrahigh-frequency oscillator and filter, thereby extending the reach of high-frequency electronics into the THz regime.

Experimental works in support of the inductive and capacitive behaviour of quantum dots are very few. Nath and his group [10] reported that CdS quantum dots embedded in SBR Latex can act as an electronic tuned circuit in the frequency range of 10–40 MHz. Some preliminary works done by Kakati et al. [11] on chemically synthesised CdS (undoped and doped) quantum dots embedded in PVA as low-pass filter are reported. In this paper, a systematic investigation of frequency response of CdS and CdS:Cu quantum dot devices, following microwave-assisted synthesis, is presented. Phase of the output relative to the input as a function of frequency is also recorded to have some insight into the observed low-pass filter characteristics of the as-fabricated samples.

2. Experimental

2.1. Synthesis and characterization

Synthesis of undoped and copper doped CdS quantum dots is carried out by microwave-assisted heating method adopted by Man et al. [12] using 3-mercaptopropionic acid (MPA) as stabiliser. The authors also reported the synthesis of MPA-capped CdS and CdS/ZnS core-shell nanoparticles using microwave-assisted synthesis process.[13] First, solutions of cadmium acetate (Cd(CH₃COO)₂) and sodium sulphide (Na₂S) are prepared
separately using de-ionised water as solvent. For undoped CdS quantum dots, these two solutions are mixed together with MPA, keeping the molar ratio of Cd\(^{2+}\):MPA:S\(^{2-}\) at 1:2:0.2 and placed inside the microwave oven for heating. The elemental weight ratio of Cd\(^{2+}\) to S\(^{2-}\) in undoped CdS is 1:0.17. For doped samples, 0.5 mM CuCl\(_2\) solution (i.e. 0.5% doping) is prepared and a few drops of this are added to the above-mentioned solution prepared for undoped sample. The composite solution is then placed inside the microwave oven for heating. The sample (undoped or doped) is then kept overnight for stabilization. Microwave-assisted heating method is used for synthesis as it requires very short reaction time and the heat distribution in the sample is very uniform. Eight undoped samples ‘S1—S8’ are synthesised with microwave power at 900 W and heating time varying from 1 to 8 min. Corresponding eight doped samples synthesised are assigned codes as ‘S1D—S8D’.

The absorption spectra of the as-fabricated samples are obtained using UV-1800 Shimadzu Spectrophotometer (190–1100 nm, spectral bandwidth: 1 nm). UV—vis spectra of some of the CdS and CdS:Cu samples are shown in Figure 1. The band-gap of the samples determined by Tauc’s equation (Table S1 of supplementary material) [14] are found to be higher than the bulk band-gap (~2.42 eV) of CdS.

The luminescence spectra of the as-fabricated samples are obtained using F-2500 Fluorescence Spectrophotometer (Make: Hitachi). PL spectra of some of the samples are shown in Figure 2. Similar results are obtained for all other samples (Table S1 of supplementary material).

The XRD patterns of the as-fabricated samples are obtained using the X-ray powder diffractometer (X’Pert pro, Make: PANalytical, X-ray tube: Cu), the same for S4 and S4D being shown in Figure 3. Broad XRD peaks at 2θ values of 26.68\(^{\circ}\), 47.8\(^{\circ}\) and 56.61\(^{\circ}\) are obtained which indicate fine size of the grains of the sample. The average crystallite size

Figure 1. Ultraviolet—visible spectroscopy of samples ‘S1—S4’ and ‘S1D—S4D’.
(D) calculated using the Debye-Scherrer equation [15] is found to be in the range of 4–15 nm.

High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) results of the as-fabricated samples are obtained using high-resolution transmission electron microscope (JEM-2100, 60–200 KV). HRTEM and SAED images for S4 are given in Figures 4 and 5, respectively.

Figure 2. Photoluminescence spectroscopy of samples ‘S1–S4’ and ‘S1D–S4D’.

Figure 3. X-ray diffraction pattern of sample (a) S4 and (b) S4D.
Figure 4. HRTEM image of sample S4.

Figure 5. SAED image of sample S4.
From Figure 4 it is clear that the particles are below 10 nm and nearly spherical in shape. From the electron diffraction pattern (Figure 5), the crystalline planes of the sample can be seen. From the HRTEM images of the samples, it is found that the average particle size of the as-synthesised samples lies in the range of 3–10 nm.

### 2.2. Device fabrication

A piece of locally available printed circuit board is taken and a portion of copper layer is etched away to get a three-electrode structure as shown in Figure 6. The sample is then deposited in thin film form between the electrodes using spin coating technique. We have modified the four-probe method to three probe one so as to obtain a common ground for both the input and output.

Coding for undoped devices is ‘DS1, DS2 …… DS8’ and for doped devices is ‘DS1D, DS2D, … DS8D’.

### 3. Results and discussion

From the UV—visible results (Table S1 of supplementary material) it is seen that for all the fabricated samples band-gap is higher than bulk band-gap of CdS (2.42 eV). Thus quantum confinement is achieved for all the samples. The table also reveals that the PL peaks for undoped samples may be due to band-edge emission and those for doped samples may be attributed to recombination of the defects and excitation states induced by Cu$^{2+}$-modified surface trap states which enhances shifts and broadens the luminescence band [16,17]; however in the present investigation broadening is not observed for S2D and S3D. XRD results (Figure 3) show the nanostructures to be of hexagonal structure with average crystallite size in the range of 4–15 nm. From HRTEM images the shape of the particles are found to be nearly spherical. From SAED it can be concluded that the diffraction is a combination of spot and rings. Thus, the material characterization results reveal that we have successfully fabricated CdS and CdS:Cu quantum dots with strong confinement having particle size in the range of 3–10 nm.
Frequency response of the devices is recorded using an arbitrary function generator (Tektronix AFG 3102, 100 MHz, 1 G.S/s) and a digital phosphor oscilloscope (Tektronix DPO 3052, 500 MHz, 2.5 G.S/s). Two pairs of recorded input and output signals on the oscilloscope for the device DS2 are shown in Figures 7 and 8, respectively.

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Observed frequency responses of the devices with undoped and doped samples are shown in Figures 9 and 10, respectively, and the phase shift versus frequency curves for undoped and doped devices are shown in Figures 11 and 12, respectively. These characteristics resemble low-pass filter behaviour. As the device fabricated consists of a large number of quantum dots having broad size distribution, the average effect of all the quantum dots on the output signal is observed.

**Figure 7.** (Colour online) Input and output characteristics of device DS2. Frequency: 50.2 Hz. Input signal (blue) voltage: 15.2 V. Output signal (yellow) voltage: 11.6 V.

**Figure 8.** (Colour online) Input and output characteristics of device DS2. Frequency: 199.6 KHz. Input signal (blue) voltage: 16.8 V. Output signal (yellow) voltage: 4.4 V.
Figure 9. Frequency response of devices DS1—DS4 and DS1D—DS4D.

Figure 10. Frequency response of devices DS5—DS8 and DS5D—DS8D.
dots may be assumed to be observed in practice. The as-fabricated device may be assumed to be composed of a number of building blocks as given in Figure 13. The central region is a quantum dot sandwiched between two potential barriers (dielectrics, being MPA for our device), $L$ being the length of the entire device such that $a \ll L$. Fu et al. [3] considering a device similar to that of Figure 13 obtained theoretically that for $|\xi| < 1$ the

**Figure 11.** Phase shift versus frequency curves for undoped devices.

**Figure 12.** Phase shift versus frequency curves for doped devices.
admittance is always inductive and for \(|\xi| > 1\), admittance of the device is capacitive at low frequencies before crossing over to and inductive behaviour at higher frequency, \(\xi\) being a parameter related to the energy and width of the resonance. Fu et al. [6] found the quantum inductance to be related to the life time of the quasi-bound state resonance level. Guided by the theoretical background given by Fu et al. [6], an equivalent circuit given in Figure 14, is suggested for the as-fabricated devices.

It is worth mentioning that the nature of the observed phase-shift versus frequency curves does not agree with those of the conventional low-pass circuits (viz. LR, CR) or LCR (of Figure 14) without the capacitor \(C_t\) in branch II. The capacitance \(C_t\) and \(C_m\) of Figure 14 are the geometrical capacitances of the as-fabricated quantum dot devices. Using OrCad capture CIS Lite software, we have simulated equivalent circuit for each of the devices by putting some random values for \(R_t, L, C_t\) and \(C_m\) to match the experimentally observed cut-off frequencies. All the recorded data of the devices as a low-pass filter are given in Table 1. The gain and phase shifts simulated are plotted in Figures 15 and 16 along with the corresponding observed characteristics for devices DS5 and DS5D.

The nature of the observed gain versus frequency and phase shift versus frequency is found to be exactly similar to those by simulations with slight deviations in the corresponding magnitudes only, for all the devices fabricated in the present work. Observed gain versus band-gap and log of cut-off frequency versus band-gap for undoped and doped devices are plotted in Figures 17 and 18, respectively. These figures reveal that both for undoped and doped devices gain and cut-off frequency have positive correlation. For
undoped devices, gain is found to be maximum in the band-gap range of 2.5–2.53 eV, whereas cut-off frequency at 2.5 eV. For doped devices both gain and the cut-off frequency are maximum in the band-gap range of 2.57–2.62 eV. Maximum phase shift versus band-gap is plotted in Figure 19 which reveals maximum phase shift to be the highest at ~2.57 eV for undoped and at ~2.63 eV for doped devices. Thus, a significant finding of the present work is that the band-gap range of 2.5–2.6 eV is crucial so far as the three important parameters, namely, gain, cut-off frequency and maximum phase shift of the low-pass behaviour of the as-fabricated devices are concerned.

At lower frequencies ac is easily passed through branch 1 consisting of $R_t$ only while at higher frequencies, $L(\omega)$ being effective (Figure 12) ac is blocked by branch 1 but passed

![Figure 15](image)

Table 1. Different recorded parameters of the samples.

| Sample code | Device code | Gain | Cut-off frequency (KHz) | Max. phase shift in degree | Frequency positions of max. phase shift in degree |
|-------------|-------------|------|-------------------------|---------------------------|---------------------------------------------|
| S1          | DS1         | 0.758| 37                      | 22.4                      | 137 kHz                                    |
| S2          | DS2         | 0.783| 16                      | 25.1                      | 55 kHz                                     |
| S3          | DS3         | 0.754| 85                      | 31                        | 400 kHz                                    |
| S4          | DS4         | 0.432| 4.5                     | 36.5                      | 8 kHz                                      |
| S5          | DS5         | 0.256| 3.6                     | 35                        | 19 kHz                                     |
| S6          | DS6         | 0.641| 12                      | 41.1                      | 30 kHz                                     |
| S7          | DS7         | 0.353| 8.1                     | 37                        | 60 kHz                                     |
| S8          | DS8         | 0.512| 17.6                    | 47.11                     | 29 kHz                                     |
| S1D         | DS1D        | 0.514| 3.8                     | 35                        | 13 kHz                                     |
| S2D         | DS2D        | 0.325| 3.82                    | 22.5                      | 20 kHz                                     |
| S3D         | DS3D        | 0.411| 6.01                    | 33                        | 18 kHz                                     |
| S4D         | DS4D        | 0.365| 4.36                    | 26                        | 11 kHz                                     |
| S5D         | DS5D        | 0.256| 2.52                    | 22.5                      | 28 kHz                                     |
| S6D         | DS6D        | 0.722| 400                     | 40.55                     | 1.2 MHz                                    |
| S7D         | DS7D        | 0.744| 640                     | 43.88                     | 1.3 MHz                                    |
| S8D         | DS8D        | 0.753| 8.2                     | 23.5                      | 22 kHz                                     |

Figure 15. Experimental (E) and simulated (S) frequency response and phase shift versus frequency for device DS5.
by branch II and also shorted at the output by $C_m$. This behaviour gives rise to the low-pass filter characteristics observed for the as-fabricated devices. As $L(\omega)$ becomes effective at higher frequencies, due to the phase delay by the quantum inductance, current, i.e. output voltage suffers a phase shift relative to the input voltage about cut-off frequency, as observed in Figures 15 and 16 for devices DS5 and DS5D.

The whole experiment for frequency response as well as phase shift variation with frequency is repeated with the device of Figure 6 replacing the nanosamples by bulk CdS as

**Figure 16.** Experimental (E) and simulated (S) frequency response and Phase shift versus frequency for device DS5D.

**Figure 17.** Gain versus band-gap and cut-off frequency versus band-gap curves for undoped devices.
well as by MPA. In both the cases, very low output is obtained without any filter behavi-our. This finding confirms that the observed low-pass filter behaviour of the as-fabricated samples is entirely due to the quantum dots embedded in MPA matrix.

Thus, the devices comprising of nano-dimensional structures and thereby following quantum mechanical charge transport mechanisms are found to simulate inductance effect at higher frequencies but no inductor is physically present in the circuit. This behav-iour is the nano-dimensional counterpart of inductance simulation of micro-electronics.

**Figure 18.** Gain versus band-gap and cut-off frequency versus band-gap curves for doped devices.

**Figure 19.** Maximum phase shift versus band-gap of undoped and doped devices.
4. Conclusion

To summarise, we have successfully synthesised CdS and CdS:Cu quantum dots. The as-fabricated quantum dot devices are found to have all the characteristics of a classical low-pass filter with optimization of gain, phase shift and cut-off frequency in the band-gap range of $2.5 - 2.6$ eV. These three parameters are found to be different for undoped and the corresponding doped devices, as by adding other materials quantum inductance and capacitance can be varied. All the quantum dots of a sample fabricated are not identical; hence, the quantum dot array may show the interplay between intrinsic effect of individual dots and properties of the dot ensemble. However, the general nature of the average behaviour is found not to deviate much from the single dot behaviour. The as-fabricated devices are tested for demodulation and satisfactory operation is observed, which suggests for employing such nanoscale devices in the field of communications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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