A Study of Nanocrystalline CdTe Type (II) Quantum Dot Based Hetero Structures

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***Abstract*- The electrical properties of nanocrystalline CdTe type II quantum dots based hetero structures deposited on conductive glass were investigated. They present interesting peculiarities. Low frequency (20 Hz ≤ f ≤ 200 kHz) dielectric properties of type II CdTe quantum dots blended with single walled carbon nanotubes (SWNTs, polyglycol functionalized) were investigated at room temperature. Negative capacitance was observed at low frequencies under forward DC biases. This phenomenon was found to result from the combinational contributions from the Maxwell-Wagner interfacial relaxation and the dipolar relaxation related to de-trapped carriers which give rise to inductive effect under an applied electric field. By using frequency dependent capacitance spectroscopy, the tunnelling effects of holes and electrons were investigated. In capacitance curves measured at low frequency, peaks were observed; these peaks could be attributed to the resonant tunnelling of charge carries into discrete energy levels of nanocrystalline CdTe and exhibit quantum confinement and Coulomb blockade effects. A clear (positive/negative) shift in capacitance-voltage(C-V) and conductance-voltage (G-V) suggests (electron/hole) trapping in nanocrystalline quantum dots.**

Keywords- Hetero Structures; Single Walled Carbon Nanotubes; Negative Capacitance; Tunnelling Effects; Nanocrystalline Quantum Dots; Quantum Confinement; Coulomb Blockade Effects

I. INTRODUCTION

It is well-known that particles within the nanoscale (<100 nm) can exhibit charge quantization similar to atoms. Nanocrystalline junctions possess amazing physical properties such as the low-frequency negative capacitance, which is observed in a variety of electronic devices like the p-n junctions, Schottky diodes & solar cells [1-5]. Negative capacitance indicates that the current variation lags behind the voltage agitation. The negative capacitance phenomenon has been ascribed to contact injection, interface states, charge trapping, space charge effect, minority-carrier injection, etc. There are two main types of interpretations suggested for the negative capacitance (or inductive behaviour). In case of the short-base p-n junction, the minority carrier depopulation at high forward bias induces a change of sign of the capacitance [6-8]. But a general interpretation of the negative capacitance (negative induction) mechanism relies upon the fact that the current between two electronic reservoirs is governed by the occupation of an intermediate state, which decreases when the applied potential increases. In the case of Schottky diodes the negative capacitance is due to the interface charge loss at the occupied states below Fermi level [9]. In the case of double-barrier resonant tunnelling diode (RTD), the quantum capacitance becomes negative in the region of negative differential resistance due to the electron charges decrease at the increasing forward bias [10,11]. The negative capacitance behaviour has been observed in a nanoscale based solar cell [12] which uses both electron and holes as carriers in such devices [13]. In this contribution it has been demonstrated that transport in CdTe type II quantum dot based devices is space-charge limited. The carrier transport properties can give information on the density of the trapping level in thin film device structures made of quantum dot (QD) composites [13] or conjugate polymers [14], which have been well characterised using space-charge limited models.

The purpose of this preliminary study is to investigate the electrical properties of CdTe/Cd S/ZnS core/shell deposited on ITO for electronic and optoelectronic devices applications [15]. For single-carrier space-charge limited (SCL) transport the current density-voltage J-V characteristic is given by the famous Mott-Gurney square law

$$J=9/8\ \varepsilon_0/\ \varepsilon\ \mu\ V^2/L^3, \tag{1}$$

with ε_0 the permittivity of free space, ε the relative dielectric constant, μ the mobility, V the applied voltage, and L the thickness. The current through [poly(p-phenylene vinylene)] based light emitting diode is three times lower than the hole current [13], and exhibits a stronger field dependence and reminiscent of traps. These traps may have resulted from contamination during processing. In another contribution on ppv based hole-only devices, an inductive contribution was observed [16] with both cathode and anode made of Au, and it was concluded that the inductive behaviour was due to dispersive transport with wide distribution in transit times.

For the present work, capacitance-frequency response was chosen to investigate the charge-carrier dynamics in CdTe type II devices. The results demonstrate that the inductive contribution is due to both electrons as well as holes. This is presumably caused by holes injected from the PEDOT: PSS [poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)] layer, and electrons injected from the Al cathode.

II. EXPERIMENTAL PROCEDURE

The devices studied consisted of a thin layer of CdTe type II quantum dots or a mixture of CdTe with SWNTs [poly(ethyleneglycol)functionalized)] sandwiched between two electrodes, Indium Tin Oxide (ITO) and Al, on top of a glass substrate. The mixture was spin-coated on the top of an optically transparent ITO electrode, followed by the spin coating of the ITO with PEDOT: PSS conductive polymer. The high work function of PEDOT: PSS makes it suitable for hole injection. The top electrode evaporated Al has a low work function and serves as the electron injector. Admittance measurements in the range of 20 Hz to 200 kHz were performed using Hameg 8118 programmable LCR bridge Impedance Analyzer. The analyzer can superimpose a bias voltage from 0 to 5 volts on top of the ac voltage V_{ac}.

The complex admittance Y is defined as the ratio of ac current and ac voltage:

$$Y = i_{ac}/V_{ac} = G + iB = G + I\,\omega C\,, \qquad (2)$$

with G the conductance, B the susceptance, C the capacitance, $i = \sqrt{-1}$, and $\omega = 2\pi f$ the angular frequency.

III. DISCUSSION OF THE RESULTS

This work focuses only on the imaginary part of the admittance, which most clearly reveals the different relaxation processes present in the device. The symmetric behaviour can be observed in its dark current-voltage variation as in Fig. 1.

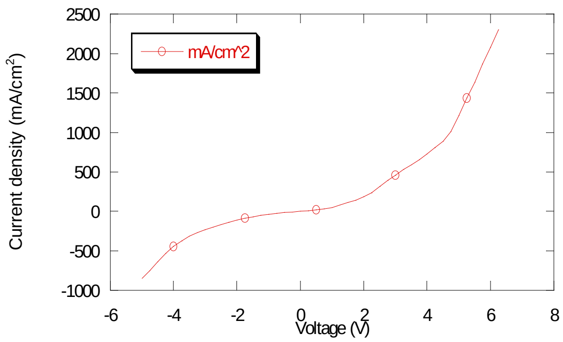

Fig. 1 Current-voltage-light plot of ITO/CdTe/CdS/ZnS core/shell/shell quantum dots spin coated/Ca-Al

In Fig.2 the frequency-dependent capacitance of the device is shown as a function of the forward bias voltage. As is evident from Fig.2, the staircase effect gets depressed when a forward bias is applied. The capacitive response and interaction of the charge carriers is slightly different due to their charges, leading to an increase in the measured capacitance higher than either with the positive biased or under magnetic field effect. The above-mentioned behaviour can be due to the double-injection that follows the space-charge conduction [17]. The slight difference in the magnitude of the capacitance may result from contamination during processing which may affect the holes in a way different to the electrons [16].

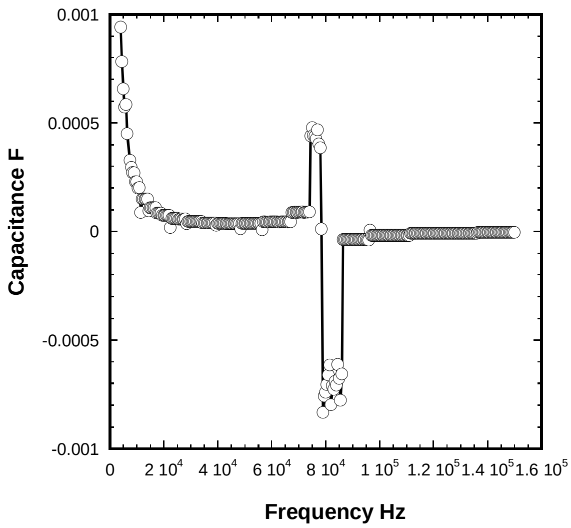

Fig. 2 Capacitance-frequency plot of ITO/CdTe/CdS/ZnS Core/shell/shell quantum dots spin coated /Al

More detailed work is required to resolve if there is any contribution from electrons to the inductive response as this material is p-type and its behaviour will be based on hole only contribution as in ppv [13]. Since both the charge carriers can contribute [17], an external magnetic field is known to interfere with the internal magnetic interaction, and this will permit the modulation of the rate constant of the dissociation process of the electron-pairs [18]. In the hole only configurations, CdSe quantum dots in [poly(3-hexylthiophene)] enhance the hole current and switch the transport from dual conduction trap and mobility models to single conduction traps model [19]. The samples deposited on electrodes with high work function (ITO, Au) are at more positively charged potential [20]. This implies that the charge exchange at the material-high work function electrode interface depends on the work function of the electrode and the charge exchange happens within a nanometer interfacial thickness region. By blending type II CdTe QDs with [poly(ethyleneglycol) functionalized], the single-walled carbon nanotubes inhibited the appearance of the negative capacitance as in Fig. 3. This is due to the interactions between the functionalized SWNTs and the QDs which modified the transport behaviour.

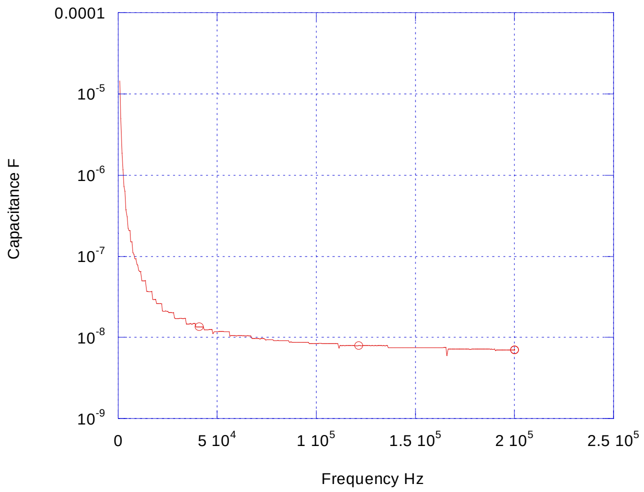

Fig. 3 Current-voltage-luminance plot of ITO/ CdTe/CdS/ZnS core/shell/shell quantum dots + SWNT [poly-(ethylene glycol) functionalized] /Al

Carbon nanotubes can be naturally n-doped to reveal n-type behaviour as was proved for the negative thermoelectric power [21,22]. Additionally, it has been found that spatially separated conduction paths of the two distinct charge carriers (electrons and holes) are induced by blending the active material with SWCNTs [23]. Lee et al. [23] have shown that the electron and hole mobilities have quite distinct dependence on the CNT concentration that the electron mobility increases gradually with the SWCNT concentration, whereas the hole mobility remains almost constant. Another group [24] concluded that the addition of SWCNTs causes faster electron transport. The results of this study suggest that adding SWCNTs restores the balance of charge carrier and gets rid of the negative capacitance in this mixture.

IV. CONCLUSIONS

The investigation in this study is related to the phenomenon of negative capacitance. This phenomenon has been displayed by a variety of electronic devices in Si, Ge and compound semiconductors, crystalline or amorphous [25]. It has been known for some time that high-level injection leads to inductive impedance for the quasi-neutral region of a pn junction [26]. Green and Shewchun pointed out that this can also happen in a Schottky junction [27]. The phenomenon has been displayed by GaAs/AlGaAs QWIP (quantum well infrared photodiode) [28-30]. Negative capacitance (NC) was reported in organic semiconductors at low frequencies [31],

However, this phenomenon appears only under bipolar injection conditions. Phenomenologically, NC effects indicate that the current variation lags behind the voltage agitation. However, the microscopic physical mechanisms of the NC in different devices are obviously different and have been ascribed to contact injection, interface states, charge trapping, space charge effect, and minority-carrier injection, etc. In practice, NC can be explained based on the behaviour of the frequency dependent admittance spectroscopy [C-V and G/ω-V] data [32].

The theory is established on the following arguments. Electrons that surmount the Schottky barrier (SB) under forward bias fill up the empty states at the interface but, because they possess excess energy when colliding with the electrons trapped, they also knock electrons out of the traps in case the binding energy of these traps is less than the SB energy [33,34]. However, to move an electron out of the interface trap into the metal, it requires much less energy than to create an electron-hole pair in bulk. The strong coupling of the trap states to the metal conduction band makes the ionization energy very different on the two sides of the interface [34]. Werner et al. [33] have shown that the complete frequency dependent admittance measurements [capacitance and conductance] enable to characterize these electrical parameters. They proposed that the observed inductive effect at a low frequency arises from the high-level injection of minor carriers into the bulk semiconductors.

The results of this study provide a potential contribution within the field of semiconductor quantum confinement and the electronic characteristics of quantum dots. This preliminary investigation may serve as a pilot study to safeguard investment for a large scale investigation.

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