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Experimental Study on Silicon Nanocrystals Rich Lanthanum Fluoride Films for Future Electronic Devices

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Abstract

Feasibility for the future electronic devices a thorough investigation on Silicon nanocrystals (Si-NCs) rich Lanthanum Fluoride (LaF3) film fabricated using a novel one-step chemical method has been reported here. Colloidal solution of Si-NCs in hydrofluoric acid (HF) was prepared from meso-porous silicon by ultrasonic vibration (sonication). On a silicon (Si) substrate $LaCl_3$ solution in HCL is allowed to react with the colloidal solution of prepared Si-NCs. $LaCl_3$ reacts with HF of Si-NCs solution and produces LaF_3 crystals that deposits on the silicon substrate as a film embedding Si-NCs. This is a novel single step chemical way of depositing LaF_3 insulating layer embedding Si-NCs (LaF_3:Si-NCs). The XRD and EDX analysis of the deposited film show a polycrystalline and non-stoichiometric nature of LaF_3. The presence of Si-NCs was confirmed by SEM. Application of this material has been tested for low-voltage operating non-volatile memory (NVM) and Schottky junction solar cells. The Al/LaF_3:Si-NCs/Al structure as NVM offered a memory window of 525 mV at a programming and erasing bias of 2V. LaF3:Si-NCs films showed strong light absorption. Current-Voltage (I-V) characteristics of the Schottky device in ITO/LaF_3:Si-NCs/Al structure showed a dependency on the incident light intensity where current was varied in the range of 5 mA to 40 mA and under various light illumination i.e., 400 lux to 1200 lux. Experimental results show a lot of promise of Si-NCs-rich LaF3 film to be used as an insulating film in non-volatile memory as well as a photoactive material in Schottkey junction solar cell.

Keywords: Hybrid-solar-cell; Macroporous; Exciton; Bulk-heterojunction; Electrochemical-etching; Fill-factor; Conversion-efficiency.

INTRODUCTION

Recently researchers have been considering nanocrystal-based memory devices as a solution to ultra-large scale integration of electronic nonvolatile memories. One major barrier to such integration of NVMs is the local defect related leakage. Using discrete nanocrystals instead of the conventional continuous floating gate as charge storage nodes, local–defect-related leakage can be reduced efficiently to improve data retention [1]. In this regard, discrete-trap type semiconductor storage materials such as Si nanocrystals (Si-NCs) embedded in a dielectric matrix have been demonstrated as potential candidates for the fabrication of high-speed, high-density, low power-consuming, and nonvolatile memories [2-6]. Therefore, the poly-silicon–oxide–nitride–oxide–silicon (SONOS)-type structure memories including nanocrystal memories have recently attracted much attention for the application in the next-generation nonvolatile memories [7], [14] because of their great potential for achieving high program/erase (P/E) speed, low programming voltage and low power performance. For conventional SONOS, erase saturation and vertical stored charge migration [13-14] are the major drawbacks; while for nanocrystal memories good enough charge keeping capability of the discrete storage nodes and the formation of nanocrystals with constant size, high density and uniform distribution are the extremely challenging issues. LaF_3 has been chosen as alternative candidates for gate insulator because of their large band gap, high dielectric constant, and large refractive index. Moreover, the lanthanide fluorides (LaF_3) show good characteristics without pre-formed interfacial layer, and regarded as high-k dielectrics [15]. In this work our goal has been to fabricate Si-NCs-rich LaF_3 film to be used as an insulating film in non-volatile memory as well as a photoactive material in Schottky junction solar cell.

EXPERIMENTAL

Colloidal suspensions of silicon nanocrystals were fabricated from porous silicon in hydrofluoric (HF) acid by sonication (Ultrasonic Vibra cell, VCX 130) at a frequency of 20 kHz. Porous Silicon (PS) samples were prepared by standard electrochemical etching in a homemade double-tank cell [**Figure-1**] of *p-type* <100> Si wafers in a HF (48%): Ethanol = 2.5: 1 solution at different current densities for 30 minutes at room light temperature and illumination.

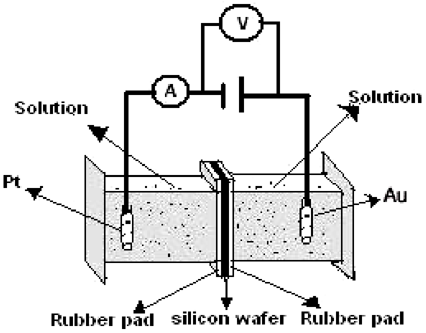


Fig-1(a)**:** Complete double-tank cell setup for PS fabrication.

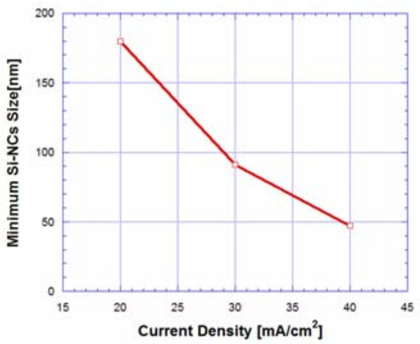


Fig-1(b) Variation of the minimum Si-NCs size with current densities

Just fabricated PS samples were readily immersed in hydrofluoric acid (HF) in a small plastic container and this container was immersed in water. Ultra sonic wave was applied to the water through the ultrasonic probe to vibrate the PS layer for about 60 minutes. The sonication was done at ultrasonic power 40 watt (amplitude~80%). The sonication crumbles the top layer of the as made PS, a weakly interconnected nanostructures network into ultra-small particles and produces luminescent, reddish, colloidal suspensions of Si-NCs. The presence of silicon nanocrystal (Si-NCs) was verified by scanning electron microscope (Models S–3400N, Hitachi). As shown in Fig-1(b) the size of the Si-NCs were dependent on the etching current density. Thus some sort of NC size tunability was obtained.

This colloidal solution of silicon nanocrystals in HF is allowed to react with Lanthanum chloride ($LaCl_3$) solution in hydrochloric acid (HCl) at room temperature on the Aluminium coated glass substrate. The chemical reaction between the $LaCl_3$ solution and colloidal solution of Si-NCs in HF can be given as

$$LaCl_3 + HF \rightarrow LaF_3 + HCl$$

The memory device was finalized by coating the top aluminium layer. For the fabrication of Schottky junction solar cell, the colloidal solution of LaF_3 with Si-NCs were made acid-free by centrifuging process using ultra cooling Sigma Laboratory Centrifuges Machine (Sigma 3K30 Centrifuge). LaF_3 with Si-NCs thin films were spin-cast onto indium tin oxide (ITO)-coated glass substrates at different rpm for different rotating times by VTC 100 Vacuum Spin Coater. Before applying colloidal solution of LaF_3 with Si-NCs on ITO coated flat glass substrate the spin coater VTC 100was programmed to spin with the specified parameters.

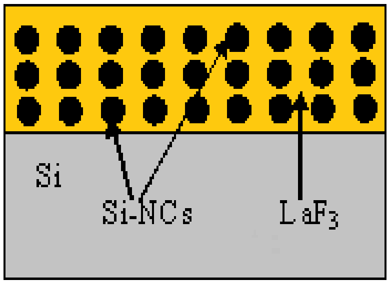


Fig - 2: Schematic diagram of a fabricated Non-volatile memory device

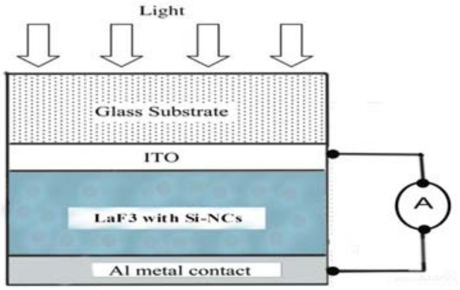


Fig - 3: Schematic diagram of a fabricated Schottky junction solar cell .

For I-V characterization of the LaF_3 with Si-NCs deposited on ITO coated glass sample, Aluminium (Al) film was deposited onto the LaF_3 films with Si-NCs. Then the copper wires were connected onto the Al and ITO layer with silver paste. The arrangement for I-V characterization is shown in [**Fig-2**].

RESULTS AND DISCUSSION

The X-ray diffraction of the deposited layer shows a polycrystalline LaF_3 deposition on silicon. Scanning Electron Microscopy (SEM) has been used to detect silicon nanocrystals (Si-NCs) embedded within the LaF_3 insulating layer and also investigated fabricated device of cross sectional view. EDX study on the LaF_3 films with Si-NCs confirmed the presence of LaF_3 and Si. As shown in fig-5 the EDX spectrum showed small carbon in the system because carbon tape were used for contact the sample with the sample stage. Table-1 shows the atom and weight percentage of various elements in the

LaF_3/Si-NCs/Si system which confirms the non-stoichiometric nature of LaF_3 deposited sample.

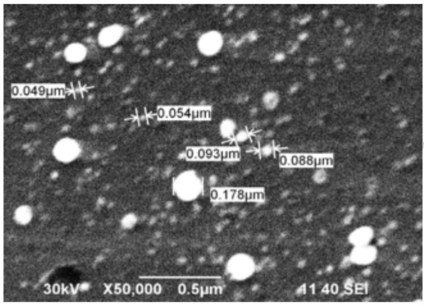


Fig-4: SEM on the LaE_3 surface

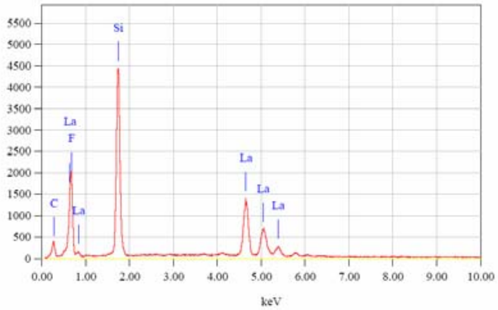


Fig-5: EDX spectra of LaF_3 films with Si-NCs

Table-1: Atom percentage of the whole system

Elements	***Weight%***	***Atom%***
C	26.40	9.63
F	21.49	25.55
Si	25.48	20.49
La	26.63	4.33

The memory measurement has been performed by an impedance analyzer. Capacitance-voltage (C-V) study of the MIS [Al/LaF_3:Si-NCs/Al] structure reveals that resonant tunneling of electron and charge storage was there when the MIS was biased from accumulation to inversion, which created a memory window. This type of memory window is called hysteresis. The MIS structure showed hysteresis for forward and reverse bias scan, enabling the structure to be used a non-volatile memory. The Capacitance-Voltage (C-V) curves observed of the LaF_3 layer deposited nonvolatile memory device for various frequencies and various bias voltage and comparative these (C-V) curves.

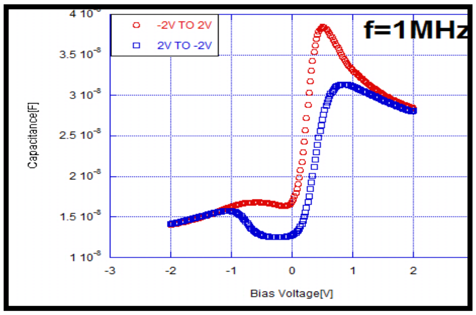


Fig-6: C-V response of Al/ LaF_3:Si-NCs /Al

The C-V characteristics were measured over a voltage range [-2V to 2V and back to -2V], [-4V to 4V and back to -4V], [-6V to 6V and back to -6V] at a room temperature with frequencies 500Hz, 1MHz, 2MHz, 3MHz, 4MHz and 5MHz. At 1MHz frequency and over a voltage range [-2V to 2V and back to -2V] hysteresis voltage difference (memory window) (525mV) is quite satisfactory **[Fig-6].** It is clearly seen from fig-6 that a memory window of about 525 mV is achievable at a bias voltage of (-2V to +2V), indicating the huge promise of the structure to be used as a non-volatile memory device.

All experimental results of optical and electrical are discussed here for 120nm of post-annealed LaF_3 films with Si-NCs. There were three [LaF_3:SiNCs/ITO/Glass] structures fabricated for optical study and each had similar performance. The optical absorption spectrum of LaF_3 films with and without Si-NCs on ITO coated glass substrate were measured and are presented in [**Fig-7**]. The LaF_3 films with Si-NCs showed strong absorption.

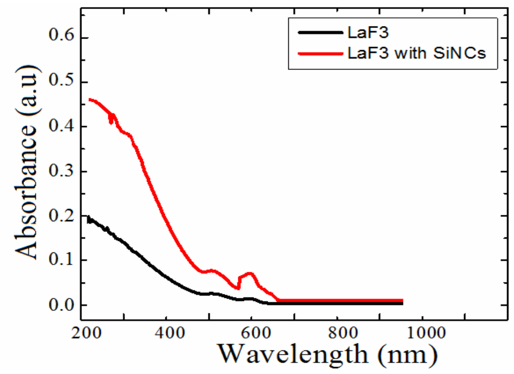
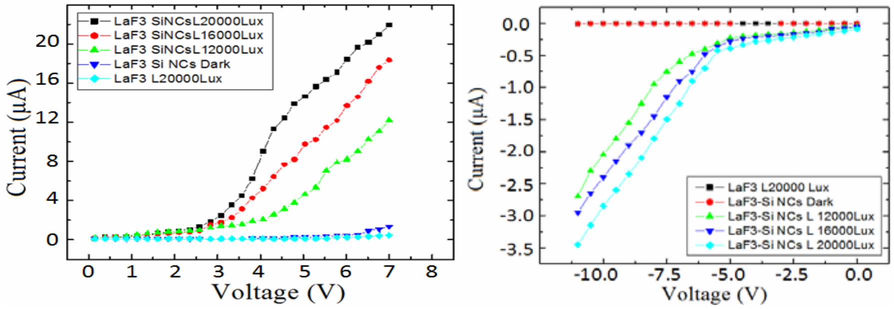


Fig-7: Absorption of LaF_3 film with Si-NCs and LaF_3 film.

The I-V characteristics of the film showed a dependency on the incident light intensity where current changed under various light illumination [**Fig-8(a) & 8(b)**]. Experimental results shows a lot of promise of Si-NCs embedded LaF_3 layer to be used as an insulating layer in MIS devices as well as a photoactive material in Schottkey junction solar cell.



(a) Forward (b) Reverse

Fig-8: Light dependent I-V response of ITO/ LaF_3:Si-NCs /Al

CONCLUSIONS

In this work, The Al/LaF_3:Si-NCs/Al structure was tested as NVM and a memory window of 525 mV was obtained at a programming and erasing bias of 2V. The LaF_3: Si-NCs films showed strong absorption.I-V characteristics of ITO/LaF_3/Si/Al structure showed a dependency on the incident light intensity where current changed under various light illumination. Experimental results show a lot of promise of Si-NCs-rich LaF_3 film to be used as an insulating film in non-volatile memory as well as a photoactive material in Schottky junction solar cell. In future, Si-NCs can be used in the conventional Si-Solar cell to enhance the conversion efficiency of solar cell.

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