Fabrication of light emitting diodes using hydrogenation-assisted nano-porous silicon thin films

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ABSTRACT

Fabrication of nanocrystalline silicon thin films using a plasma-assisted hydrogenation technique is reported. A MOS-like structure was used for realization of light emitting diodes (LEDs) and the electrical behavior of the device was analyzed. The films show photon emission in the visible wavelength regime due to quantum confinement effects. The electrons tunnel through a thin titanium oxide layer and recombine with the holes provided by the p-type substrate so the I-V characteristics show rectifying behavior in the forward bias. The quality of this heterostructure device was measured by high frequency C-V analysis. Moreover, band bending at the interface of nc-Si and oxide makes the structure a promising candidate for BiCMOS transistors.

Keywords: nano-crystalline silicon, light emitting diode, plasma assisted hydrogenation, MOS-like structure

1 INTRODUCTION

It is well known that silicon is the most important material in semiconductor technology but is not suitable in its bulk form for the fabrication of optoelectronic devices due to its indirect band-gap. Since Canham [1] reported visible photoluminescence of porous silicon at room temperature, a significant effort has been made to develop efficient light-emitting devices based on nano-porous silicon layers. One of the most utilized methods for producing nano-porous silicon layers is based on anodization of the silicon wafers in a HF and methanol/H_2O solution which can be accomplished with [2] or without [1, 3] the presence of incident light. This method resulted in rod-like structures with photoluminescence over the visible spectrum [4] and red-NIR electroluminescence [5]. This technique, however, suffers from incompatibility with standard silicon fabrication technology, mostly due to a wet chemical processing step.

In an effort to make the fabrication of porous silicon more compatible with existing silicon technology, an ion implantation of silicon in the SiO_2 or Si_3N_4 approach has been developed [6-8] which shows excellent photo-luminescence resulting from a quantum confinement effect. Despite the proper control of the size and distribution of the grains with this technique, it is rather expensive and requires high-dose implantations. On the other hand, the fabricated optoelectronic devices with this method suffer from current injection problems due the presence of a thick insulating layer and high-dose implantation is required to improve the conductivity. Other methods for producing porous silicon such as high-temperature annealing of the amorphous silicon layers and arc-discharge methods have also been reported.

In this paper, we report an inexpensive and controllable method for the fabrication of nanocrystalline-Si (nc-Si) using a DC plasma hydrogenation and annealing technique. The plasma hydrogenation step is compatible with existing standard silicon technology without causing any damage to the silicon substrate. The formation of nano-crystalline structures is believed to be due to the energy imparted to the silicon atoms as a result of the hydrogenation and de-hydrogenation sequence.

2 DEVICE FABRICATION

Fifteen Ω-cm P-type Si (001) substrates were cleaned using RCA #1 solution and blown dry in air. The cleaned substrates were then placed in an RF sputtering unit where a 200 nm thick amorphous silicon layer was deposited in an argon atmosphere at a plasma power of 350 W. The as-deposited samples were then placed in a DC-PECVD reactor for three consecutive hydrogenation and annealing steps. The hydrogenation step was performed at different plasma powers and temperatures, and the subsequent annealing step was performed at a temperature 70 ^oC higher than the hydrogenation step with the plasma power turned OFF. Three hydrogenation and annealing steps were found to be optimal in forming nc-Si grains and no significant improvement in the light-emitting properties of the layers were observed by a further repeat of these processing steps. It is believed that in the process of hydrogenation, hydrogen radicals replace the dangling bonds of the Si atoms in the amorphous structure and when depassivating the previously hydrogenated bonds, energy is transferred to the silicon atoms enhancing the chance for nucleation and growth of the nano-crystals. The samples were hydrogenated using a

plasma power density of 2 W/cm^2 and the hydrogenation / annealing process was performed in 3 sets of 30 minutes each. Decreasing the plasma power density led to a denser distribution of nano-crystalline silicon islands, whereas shorter time intervals did not completely crystallize the amorphous silicon layer resulting in the formation of crystalline islands surrounded by a "sea" of amorphous silicon. The hydrogenation and subsequent annealing steps were performed at 300 ^{o}C.

Next, the samples were placed in a CVD reactor and 15 nm of TiO_2 was deposited on the surface followed by 50 nm of indium-tin oxide (ITO) deposited by RF Sputtering in an argon atmosphere at a plasma power of 150 W. The samples were then treated at 300 ^{o}C in order to increase the conductivity and transparency of the ITO layer in the visible wavelength regime [8]. Patterned gold and copper layers were deposited for use as top and bottom contacts, respectively, and the complete fabrication process starting from the substrate to the fabrication of an LED is shown in Fig. 1.

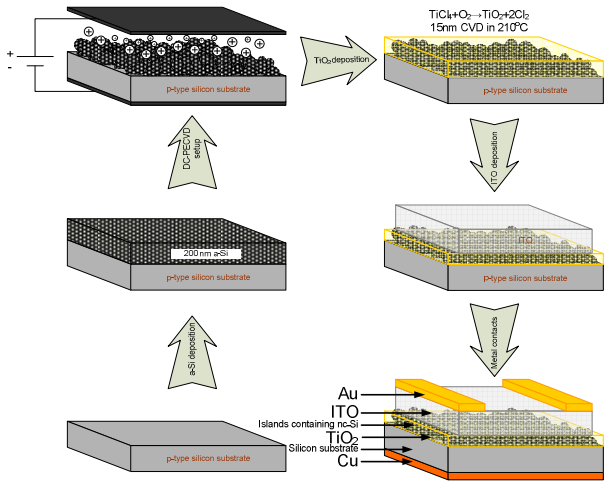

Figure 1: Process flow diagram of the method used to form an LED structure.

3 RESULTS AND DISCUTIONS

Fig. 2 presents a planview SEM image of a prepared sample displaying islands that are hundreds of nanometers in diameter and containing silicon crystals with diameters on the order of nanometers. The islands are relatively uniform in size and the 3D structure of the grains is highlighted in the inset image of Fig. 2. Each island is formed from the agglomeration of smaller particles containing nano-sized crystalline silicon dots.

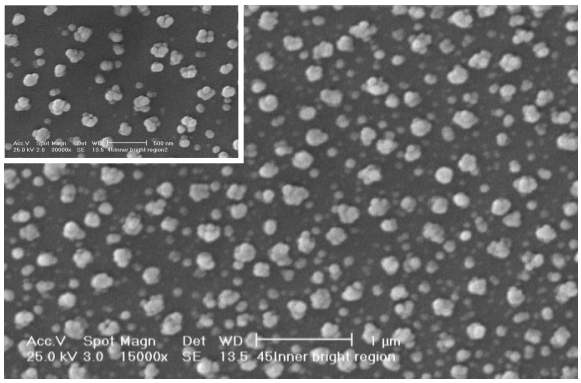

Figure 2: SEM image of silicon islands after the hydro-genation and annealing steps. Inset: a higher resolution image showing the 3D structure of the porous silicon.

A bright-field TEM image of one of these islands in cross section is shown in Fig. 3. Formation of nano-sized crystalline grains in the amorphous matrix is shown.

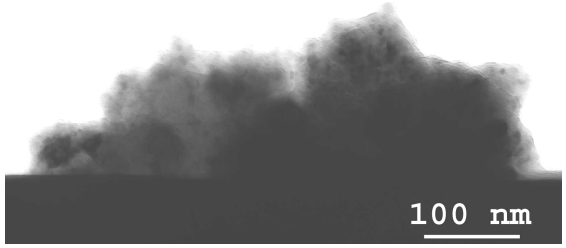

Figure 3: Bright-field TEM cross-section image of one silicon island.

A dark-field TEM image of the same sample is presented in Fig. 4 and the nano-crystalline structure of island is readily observed. Future work will concentrate on controlling the power density and time of hydrogenation process, as well as the annealing sequences so that more uniform sized nano-crystals can be prepared. A selected area diffraction pattern of the same sample is inset in Fig. 4 confirming the poly-crystalline nature of the island.

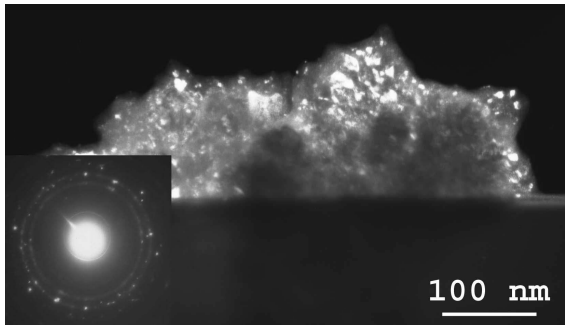

Figure 4: A dark-field TEM cross-section image of a silicon island. Inset: The selected area electron diffraction pattern obtained from this island.

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A high-resolution TEM image from a small region of the sample shown in Fig. 3 and 4 is presented in Fig. 5. Visible in this picture are lattice fringes from some of the nano-crystals due to the {111} lattice planes of silicon. These islands are located in different crystallographic orientations and tilting the specimen will result in the observation of fringes from a different set of nano-crystals.

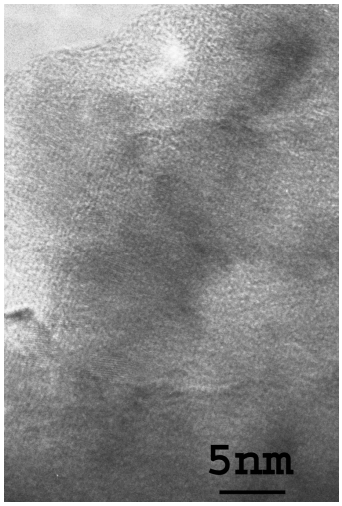

Figure 5: High-resolution TEM image from a small region of a silicon island.

The samples were studied by cathodoluminescence (CL) in order to demonstrate the optical emission properties of the nc-Si films. Fig. 6 displays sample spectra from three different specimens which show various peak wavelengths in the visible regime. It is believed that the blue emission is due to defects in the native oxide on nc-Si layer. The green and red light are believed to be due to quantum confinement effects.

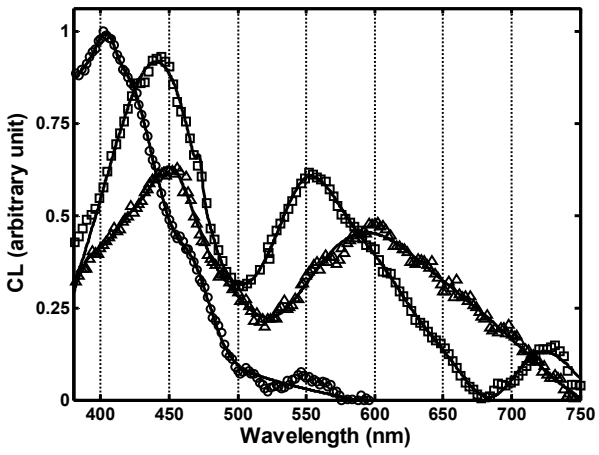

Figure 6: CL spectra from three different samples. (○–2 W/cm^2, 200 ˚C; □–2.5 W/cm^2, 400˚C; Δ-2.5 W/cm^2, 350˚C)

Fig. 7 shows the I-V characteristics of the fabricated device and shows rectifying behavior which is consistent with the MOS model. Electrons can tunnel through the thin TiO_2 layer in the forward bias condition and the rectifying manner is believed to be due to the presence of a depletion region at the nc-Si – oxide interface as presented in Fig. 8. Band bending in the nc-Si – oxide region prevents current flow when reverse biased.

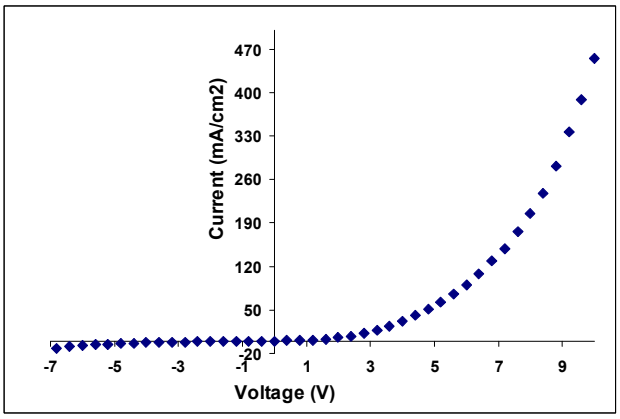

Figure 7: I-V characteristic of the final device.

The high frequency C-V characteristic of the structure is shown in Fig. 9 and a MOS-like behavior is observed. By increasing the voltage of top electrode, around the threshold voltage, the total capacitance decreases to the minimum value and then plateaus at this value.

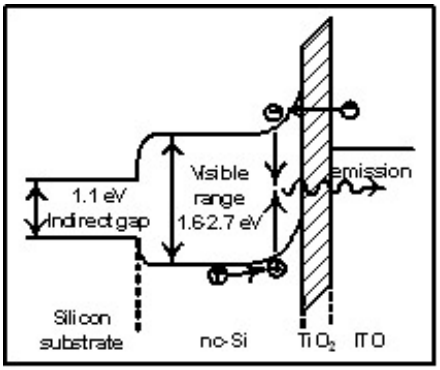

Figure 8: The proposed energy level diagram of nano-crystalline silicon with respect to silicon substrate energy bands

This high-frequency characteristic can be explained by considering our proposed energy diagram model shown in Fig. 8. The energy gap difference between the P-type Si substrate and the nc-Si layer restricts the direct transfer of charge between these two layers, so the nc-Si layer acts as an insulator and the initial value of the total capacitance represents the constant capacitance of the nc-Si and thin TiO_2 layers. By increasing the voltage on the top electrode,

the electric field penetrates through the lightly boron-doped Si substrate and extending the width of the depletion region. Hence, the overall capacitance decreases to reach its minimum value at the point of maximum depletion width inside the Si substrate.

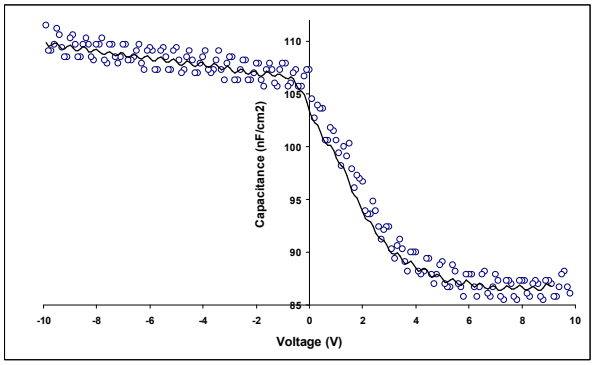

Figure 8: High frequency C-V characteristic of the final device.

This technology is also promising for the fabrication of a BiCMOS structure where bipolar and CMOS transistors are included on a single chip. Bipolar transistor performance might be achieved by implanting the nc-Si into the oxide layer and will be the focus of future studies.

4 CONCLUSION

In conclusion, we have successfully fabricated light-emitting layers and diodes by using a hydrogenation/annealing technique to create nanometer-sized crystals from a deposited amorphous silicon layer. LEDs were prepared by depositing layers of TiO_2 and ITO on top of the nc-Si layer, and rectifying behavior was observed. Devices displaying better rectifying behavior also displayed superior light emission properties. In addition, the electrical characteristic of the nano-crystalline layer is promising for the fabrication of a BiCMOS device.

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