Optoelectronic Characteristics of Hydrogen and Oxygen Annealed Si/O Superlattice Diode

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Optoelectronic characteristics of the superlattice diode as a function of deposition temperature and annealing conditions have been studied. The multilayer nanocrystalline silicon/adsorbed oxygen (nc-Si/O) superlattice formed by molecular beam epitaxy (MBE) system. Experimental results showed that deposition temperature of 550 °C, followed by hydrogen annealing leads to best results, in terms of optical photoluminescence (PL) and electrical current-voltage (I-V) characteristics. Consequently, the experimental results of multilayer Si/O superlattice device showed the stable photoluminescence and good insulating behavior with high breakdown voltage. This is very useful promise for Si-based optoelectronic devices, and can be readily integrated with conventional silicon ULSI processing.

Keywords: photoluminescence (PL), nc-Si/O superlattice, Raman scattering, resonant tunneling.

1. INTRODUCTION

Silicon is the cornerstone material in conventional VLSI systems. However, having a relatively small and indirect fundamental energy band-gap, silicon is an inefficient light-emitter. On the other hand, direct integration of III-V photonic materials on a silicon chip is still very problematic. Light out of silicon itself appears to be an attractive alternative. Light emission from silicon is an important fundamental issue with enormous technological implications. R. Tsu and L. Esaki introduced the concept of man-made superlattices thirty years ago [1, 2]. After that, the use of nanoscale silicon particles imbeded in an oxide matrix was introduced [3, 4] for possible silicon quantum devices operated at room temperature. A diode structure with annealing and oxidation of a thin amorphous silicon layer sandwiched between oxide layers, followed by a proper electrical forming process [5], was reported several years ago. It is noted that electrical forming is essential for the minimization of possible breakdowns with high electric fields [6], as well as serving as a selection of particle sizes. Recently, R. Tsu et. al. reported a new type of superlattice is formed by replacing the heterojunction between semiconductor layers by a monolayer of adsorbed species such as oxygen atoms, and CO, molecules [7, 8]. The evidences of resonant tunneling via nanocrystalline silicon sandwiched in an adsorbed oxygen monolayer

(ML) are confirmed from those work.

In this work, the optoelectronic characteristics of multilayer nanocrystalline epitaxially grown silicon/adsorbed oxygen (nc-Si/O) superlattice have been studied to investigate several possibilities towards developing silicon-based optoelectronic devices. The electrical I-V and PL characteristics of superlattice diode as a function of the different deposition temperature and annealing conditions have been presented. Consequently, the experimental results of multilayer Si/O superlattice device showed the stable photoluminescence and good insulating behavior with high breakdown voltage. This is very useful for Si-based optoelectronic devices, and can be readily integrated with conventional silicon ULSI processing.

2. EXPERIMENT

Multilayer nc-Si/O superlattice were prepared in an ultra high vacuum (UHV) molecular beam epitaxy (MBE) system, with a growth chamber base pressure of $\sim 10^{-10}$ Torr. Antimony (Sb) doped buffer silicon of 20 nm was deposited with electron beam onto a single crystalline n-type (100), $\rho \approx 0.01$ - 0.1 $\Omega \cdot \text{cm}$ silicon substrate. The samples were grown at various temperature, room temperature (RT), 300 °C and 550 °C, and at a low growth rate with 0.5 Å/second. After the buffer layer is completed, oxygen is introduced into the

growth chamber, which allows precise control of the oxygen flow. Typically, the oxygen exposure is increased to 100 Langmuir (1L is defined as an exposure to oxygen for 100 seconds at 10^{-8} Torr). After the oxygen exposure is completed, the substrate temperature is then increased to 550 °C for deposition of the first silicon layer. Typically, 1.2 nm of undoped silicon is deposited with an electron beam source. This process is repeated and a total of nine period Si/O superlattice were grown. Finally, an antimony doped $4 \sim 5$ nm silicon layer is deposited on top of the nine periods for capping the superlattice and facilitating the deposition of the electrical contact.

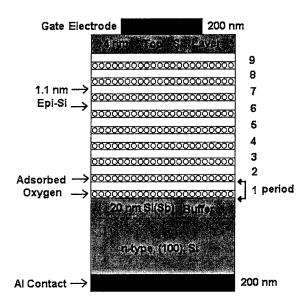


Fig. 1. Schematic cross sectional structure of nc-Si/O superlattice device.

After the MBE deposition is completed, the sample is usually cut into several pieces for further processing. To investigate the electronic and optical characteristics as a function of annealing conditions, the samples were annealed in $H_2 + N_2$ (1:10) at 420 °C for 10, 20, 30 minutes, respectively. The another sample was annealed in O₂ + N₂ (2:1) at 800 °C for 10 minutes. Hydrogen gas used for the passivation of dangling bond defects, while nitrogen serves as forming gas. Finally aluminum (Al) electrode of 200 nm thickness is deposited on the top side of the wafer, by means of thermal evaporation, at 10⁻⁷ Torr. The devices are completed by deposition of a 200 nm aluminum contact on the backside of the wafer. The spectra of PL was obtained with a U-1000 Yvon-Jobin monochrometer and detected with a R-943 Hamamatsu photo-multiplier tube (PMT). The 457.9 nm line of the LEXEL argon (Ar) ion laser was used for the PL spectra. The dc I-V measurements were performed with a Keithley 236 I-V system. Fig. 1 gives a schematic view of the device used for the I-V and G-V measurements, having contact area $\sim 10^{-3}$ cm².

3. RESULTS AND DISCUSSION

As-deposited samples exhibit either very weak, or no photoluminescence at all. Raman scattering shows that silicon deposited at room temperature remains amorphous. The samples were cut into several pieces, and were annealed under various conditions, hydrogen annealing at 420 °C and oxygen annealing at 800 °C, respectively.

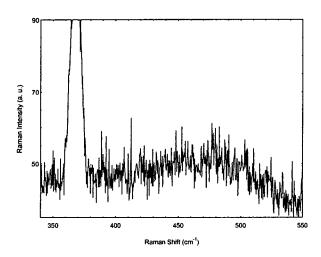


Fig. 2. Raman scattering spectrum of as-deposited Si/O superlattice sample.

Fig. 2 shows Raman scattering using the 457.9 nm argon (Ar) ion laser line of as-deposited sample. A typical Raman spectrum of amorphous silicon, having a broad peak at 480 cm⁻¹ is observed. After annealing at 800 °C, for 20 min. in oxygen and nitrogen, a Raman peak characteristic of nanocrystalline silicon appears. Fig. 3 shows Raman spectrum after annealing, peaking at 516 cm⁻¹. Since hydrogen passivation appears to be important for strong light emission, the photoluminescence was examined as a function of annealing conditions.

Fig. 4 shows photoluminescence spectra of a sample grown at 550 °C. The sample was annealed in hydrogen at 420 °C for 10 minutes, and in oxygen at 800 °C for 10 minutes, respectively. As shown in Fig. 4, the photoluminescence of hydrogen-annealed sample was quite stronger, which is indicating a better quality of passivation. It is known, that although oxygen can also provide some passivation, hydrogen passivation is essential for efficient luminescence [9]. Fig. 4 also

shows that the photoluminescence spectrum of the oxygen annealed sample is blue shifted by approximately 250 meV, indicating a further reduction in the particle size as a result of oxygen annealing. After establishing the importance of hydrogen annealing for efficient luminescence, we proceeded to examine the role of the crystallinity of the silicon cluster in the luminescence.

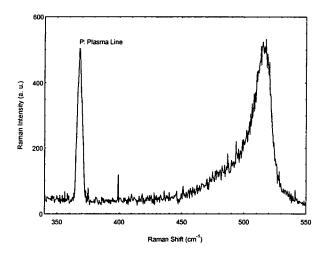


Fig. 3. Raman scattering spectrum of oxygen annealed Si/O superlattice sample at 800 °C.

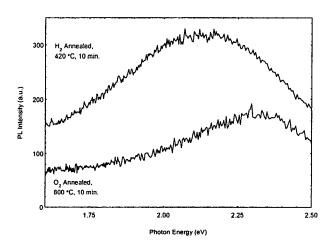


Fig. 4. Photoluminescence spectra of Si/O superlattice samples grown at 550 °C, annealed in hydrogen and oxygen, respectively.

Fig. 5 shows the PL spectra for three samples deposited at three temperatures; room temperature (RT), 300 °C and 550 °C. All samples were annealed in hydrogen, at 420 °C for 20 minutes. The crystallization of such thin layers is restricted by the proximity of the adjacent adsorbed oxygen gases. The silicon remains primarily amorphous state at room temperature deposition and 420 °C hydrogen annealing. Raman

scattering shows only partial crystallization. Therefore it is expected for the photoluminescence spectra to be blue shifted. In fact, our PL peak at 2.3 eV photon energy, compares closely to that reported in reference [10]. The photoluminescence from the sample deposited at 550 °C is red shifted. This red shift can be explained in terms of increased crystallization, and subsequent increase in the cluster size. Raman scattering shows significant crystallization for this sample. In addition, note that the photoluminescence intensity for the 550 °C grown sample is quite higher, indicating that crystallization leads to stronger luminescence. The photoluminescence spectrum of the sample grown at 300 °C appears to be intermediate, both in photon energy peak and in photoluminescence intensity. The above analysis from Fig. 4 and Fig. 5 indicates that quantum confinement gives rise to a greater blueshift for smaller crystallites. That is, the blueshift in the PL peak of the sample with oxygen anneal, compared to the sample with hydrogen anneal, is due to a contribution from smaller crystallites.

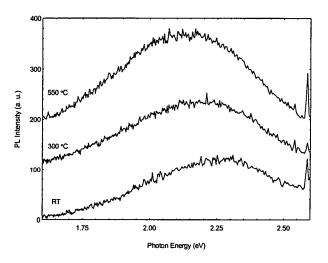


Fig. 5. Photoluminescence spectra of three nine period nc-Si/O superlattice samples grown at 550 °C, 300 °C, and 25 °C respectively. All samples were annealed in hydrogen and nitrogen, at 420 °C for 20 minutes.

Fig. 6 shows the comparison of the I-V characteristics for 420°C, 30 minutes hydrogen annealed and 800 °C, 10 minutes oxygen annealed samples. The device is stable at bias voltage up to +30V and -30V. Inset figure shows the I-V characteristics for the same type of samples with a smaller ranges, -5V and +5V, of bias voltage. It is important to point out the difference between this work and those reported previously [11, 12]. The previous single barrier results in a rather unsymmetrical I-V because the schottky barrier formed by the aluminum on Si dominates [11], whereas both I-V in Fig. 6 are quite symmetrical because a relatively high

n-doped Si is between the Al contact and the superlattice structure under investigation. Up to a bias of 30V, there is no sign of breakdown, which is indicate that our multilayer Si/O superlattice barrier can serve as an isolation for Si devices. However, the low voltage isolation is not quite sufficient for implementation as a substitute for silicon-on-insulator (SOI). This thick barrier may be useful as an epitaxial insulation gate for field effect transistor (FET). The rationale is that it should be possible to fabricate an FET on the top of another, moving one step closer to the ultimate goal of a 3-dimensional integrated circuit, 3D-IC.

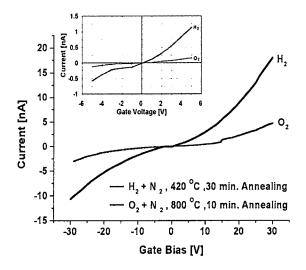
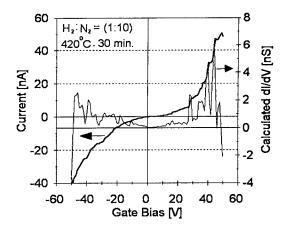
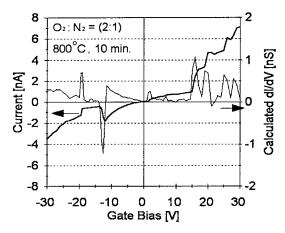


Fig. 6. Current versus bias voltage for two samples, H_2 for 420°C, 30 minutes hydrogen annealed and O_2 for 800°C, 10 minutes oxygen annealed samples. Inset figure shows I-V for the same same type of samples with a smaller ranges, -5V and +5V, of bias voltage.

Fig. 7(a) and 7(b) show the I-V and dI/dV of the detailed comparison of the H2 and O2 annealed cases. There is negative conductance which is probably due to hot carrier injection into the silicon capping region and the silicon buffer region undergoing avalanche multiplications as discussed in previous publication [13]. Probably resonant tunneling via some inadvertant isolated defects are responsible for the initiation of the process. The details of the I-V and dI/dV are really far more complex. Simple explanation based on resonant a model including trapping tunneling without mechanisms cannot offer a satisfactory understanding at this point. The appearance of jumps and negative resistance indicates the presence of electrically active defects and traps, which may be reduced by further investigation involving passivation and optimization of parameters, such as the thickness of the thin silicon as well as the oxygen exposure.



(a) 420°C, 30 minutes hydrogen annealed sample.



(b) 800°C, 10 minutes oxygen annealed sample.

Fig. 7. I-V characteristics and the calculated dI/dV c haracteristics; (a) 420°C, 30 minutes hydrogen annealed samples, (b) 800°C, 10 minutes oxygen annealed samples. The all curves were replaced for clarity.

4. CONCLUSIONS

The optoelectronic characteristics of superlattice diode as a function of deposition temperature and annealing conditions have been studied. The multilayer nanocrystalline silicon/adsorbed oxygen (nc-Si/O) superlattice formed by molecular beam epitaxy (MBE) system. Raman scattering measurement was performed to confirm the presense of nanocrystalline Si structure. The blueshift was observed in the photoluminescence (PL) peak of the oxygen annealed sample, compared to the hydrogen annealed sample, which is due to a contribution from smaller crystallites. The currentvoltage (I-V) characteristics for hydrogen- and oxygenannealed samples were quite symmetrical, and up to a bias of +30V and -30V, the device was stable. Also,

the dI/dV characteristics showed jumps and negative conductance, which is due to electrically active defects and traps. This results will guide a step in the right direction for the fabrication of silicon based optoelectronic and quantum devices as well as for the replacement of silicon-on-insulator (SOI) in high speed and low power silicon MOSFET devices of the future.

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REFERENCES

- [1] L. Esaki and R. Tsu, IBM J. Res. and Develop., vol. 14, p. 61, 1970.
- [2] R. Tsu and L. Esaki, Appl Phys. Lett., vol. 22, p. 562, 1973.
- [3] D. Babic, R. Tsu, and R. F. Greene, "Ground-state energy of one- and two-electron silicon dots in an amorphous silicon dioxide matrix", Phys. Rev., B45, p. 14150, 1992.
- [4] Q. Y. Ye, R. Tsu, and E. H. Nicollian, "Resonant tunneling via microcrystalline-silicon quantum confinement", Phys. Rev., vol. B44, p. 1806, 1991.

- [5] E. H. Nicollian and R. Tsu, "Electrical properties of a silicon quantum dot diode", J. Appl. Phys., vol. 74, p. 4020, 1993.
- [6] S. Y. Chou and A. E. Gordon, "Steps and spikes in current-voltage characteristics of oxide/microcrystallite-silicon/oxide diodes", Appl. Phys. Lett., vol. 60, p. 1827, 1992.
- [7] R. Tsu, "Silicon-based quantum wells", Nature, vol. 364, p. 19, 1993.
- [8] R. Tsu, A. Filios, C. Lofgren, K. Dovidenko, and C. G. Wang, "Silicon epitaxy on Si (100) with adsorbed oxygen", Electrochem and Solid State Lett., vol. 1(2), p. 80, 1998.
- [9] R. Tsu, E. H. Nicollian, and A. Reisman, "Passivation of defects in poly crystalline superlattices and quantum well structure", Appl. Phys. Lett., vol. 55, p. 1897, 1989.
- [10] Z. H. Lu, D. J. Lockwood, and J. M. Barlbeau, "Quantum confinement and light emission in SiO₂/Si superlattice", Nature, vol. 378, p. 258, 1995.
- [11] J.Ding and R. Tsu, "The determination of activation energy in quantum wells", Appl. Phys. Lett., vol. 71, p. 2124, 1997.
- [12] R. Tsu, A. Filios, J.C. Lofgrene, D. Cahill, J. Vannostrand, and C.G. Wang, "An epitaxial Si/SiO2 superlattice barrier", Solid-state Electronics, vol. 40, p. 221, 1996.
- [13] R. Tsu, "Room temperature silicon quantum devices", International J. High Speed Electronics and Systems, World Scientific Publ. Co. Vol. 9, p. 145, 1998.