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13. ABSTRACT (Maximum 200 words) Two schemes were studied: (1) IAG-Superlattices (Interface-Adsorbed-Gas) were fabricated in a silicon MBE system capable of exposure to oxygen at 10^{-7} Torr for adsorption. Si deposition is between 5 to 20nm at room temperature with annealing temperature between 800 to 950C, forming 3nm Si nano-particles. Photoluminescence shows two peaks located at 1.7eV and 2.35eV. The former originates from the interior, whereas the latter from the surface regions of the silicon nano-particles. (2) Si/O Superlattices were fabricated with silicon epitaxial growth (1.1nm) at 550-600C, followed by oxygen adsorption at room temperature. High resolution TEM shows epitaxy, and Plane view TEM shows defect densities, dislocations and stacking faults, below $10^9/cm^2$. The process is repeated up to 9 periods for photoluminescence, PL, and electroluminescence, EL, measurements. A broad peak located at 1.8eV, originates from quantum confinement in silicon thin layers, and a sharp peak located at 2.2eV, originates from the Si/O complexes. EL is particularly impressive. Greenish light output is stable in a life-test of more than one year of continuous operation. Our results stimulate new views toward physical phenomena originated from interfaces and surfaces:" the overall control and resulting stability allow such devices to be ready for applications."			
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Summary :

Because of the indirect fundamental energy bandgap, silicon, the overwhelmingly dominant electronic material has not played a role in optoelectronic devices. Furthermore, unlike compound semiconductors such as GaAs, InP, etc., where lattice matched heterostructures are available for quantum devices such as superlattices and quantum wells, germanium is the only known material forming heterojunction with silicon. However, the structure is really not a silicon device because the carriers are confined in germanium, not in silicon. The lack of a direct energy bandgap may be overcome by quantum confinement in a nano-particle such as in porous silicon, PSi. [1] We have developed a scheme, IAG-Superlattice (Interface Adsorbed Gas) involving silicon nano-particles arranged in a multilayer structure separated by adsorbed oxygen. And the lack of a heterojunction may be overcome by a scheme using a monolayer of oxygen, in between epitaxially grown thin silicon layers, the Si/O Superlattice. [2] These possibilities were explored in this work supported by ONR. To a surprisingly large degree, both schemes - using nano-particles of silicon, and using monolayers of oxygen between adjacent silicon layers, are fruitful. The photoluminescence, PL, from the IAG Superlattice shows two peaks, located at 1.7eV and 2.35eV. Both PL and EL (electroluminescence) devices have been achieved with the Si/O Superlattice operating continuously for over one year with stable light output. These results show that an all silicon light emitting device is at hand.

IAG Superlattices

Interface Adsorbed Gas Superlattices were fabricated with the following steps:

- (1) Deposition of amorphous silicon, a-Si, 5-20nm thick on quartz substrate at room temperature.
- (2) Introduction of oxygen adsorption followed by repeat of a-Si deposition.
- (3) Repeat the process until reaching the desired number of periods.

(4) Annealing at 800-950C in a mixture of oxygen, hydrogen and nitrogen.

PL is measured with an Ar laser (457.9nm). There are two peaks: 1.7eV and 2.34eV. It was found that the 1.7eV peak originates from the interior portion of the silicon nanoparticles, and the 2.34 eV peak originates from the outer surface region of the silicon nanoparticles.[3,4,5] Figure 1 shows the typical spectra of a 9-period Si/IAG superlattice with period $d = 10\text{nm}$. The average size of the silicon nanoparticles is 3nm determined by Raman scattering and TEM. The efficiency of our Si/IAG samples is comparable to porous silicon. It is worthy of note that PSi has insurmountable problems with poor morphology and mechanical robustness. Our samples are mechanically robust. EL is not as stable as our second scheme involving epitaxial layers of silicon separated by monolayers of adsorbed oxygen. For this reason, we have not pursued an EL device with the Si/IAG superlattice. In PSi, the PL spectrum consists of one part originating from the quantum confinement of silicon, and a blue component originating from the silicon oxygen complexes. The origin of emission in our case is very similar, even the spectrum is similar.

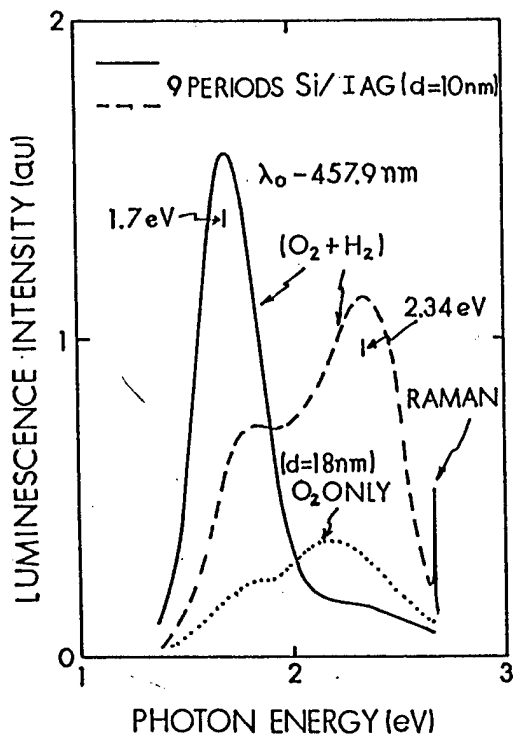


Fig. 1 PL versus photon energy excited by the 457.9nm Ar laser line. ($\text{O}_2 + \text{H}_2$) indicates annealing in a N_2 atmosphere containing both oxygen and hydrogen.

Si/O Superlattices

Several years ago, it was proposed that silicon epitaxy may be possible beyond an adsorbed monolayer of oxygen.[2] Under this grant, we have first proceeded to fabricate a

multilayer structure with silicon MBE, epitaxially grown at relatively low temperature, followed by adsorption of oxygen at near room temperatures. It was found that epitaxy is indeed continued after exposure to oxygen. Figure 2 shows a typical high resolution TEM taken from Ref.[6]

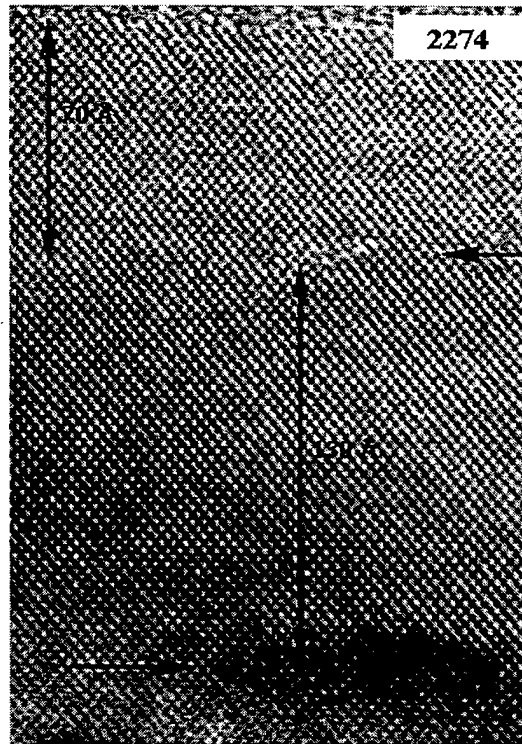


Fig.2 High resolution X-TEM (Middle arrow shows O/Si/O cluster)

A structure involving two adsorbed oxygen with 1.1nm of silicon in between shows a barrier height up to 0.5eV measured by the use of Arrhenius plot of the tunneling current at a range of applied voltages.[4,7]. Results show that the barrier height is basically given by the lowest quantum well state of the double barrier structure.[8] In this case the 1.1nm silicon is the quantum well and the adsorbed oxygen monolayers on both sides constitute a double barrier structure. We shall discuss the effective barrier height of the silicon-oxygen complex later in this report.

The measured PL and EL spectra are shown in Fig.3. [9,10] For EL, a partially transparent thin gold contact is used. We have tested several device with 4-periods and 9-periods. The actual photograph of the EL device is shown in Fig.4. [9,11] It is not possible to show the actual PL device because the laser light overwhelms the photoluminescence. We have tested an EL device continuously for over one year. Not only that the output is stable, the voltage needed to maintain the output is reduced from -10.4V voltage to -6.8V volts indicating

that some sort of annealing has taken place which reduced some non-recombination defect centers.

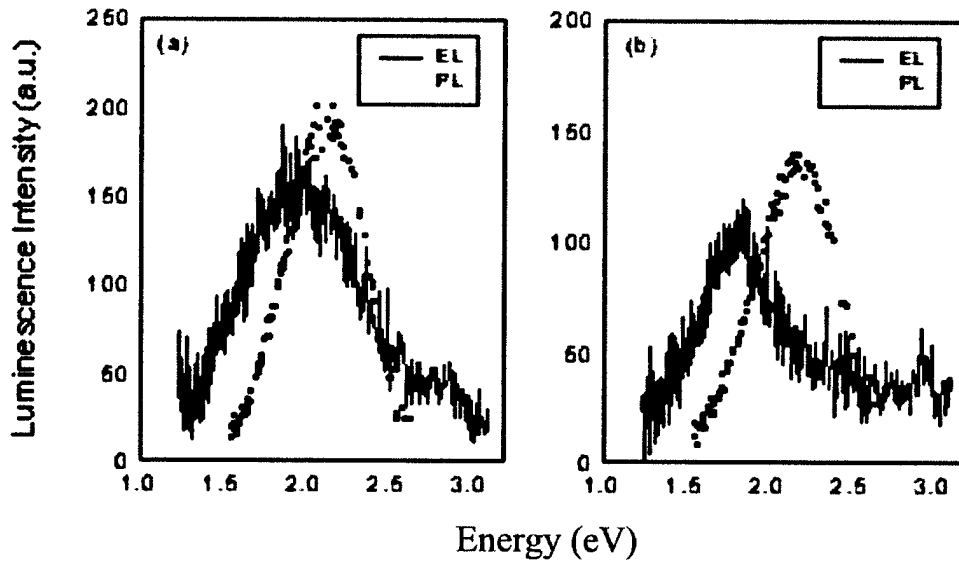


Fig. 3 The EL and PL spectra measured at room temperature of (a) sample 1 at reverse bias $V=14$ V, and (b) sample 2 at reverse bias $V=20$ V. The applied voltage includes the voltage drop over the substrate. The EL extends beyond the 457.9nm Ar laser line, used for the excitation of PL

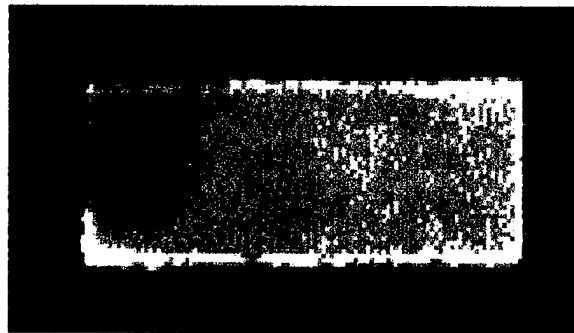


Fig. 4 EL of a 9-period Si/O with partial transparent Au for electrode, 0.5×1.2 mm. The dark area is caused by the contact wire vignetting part of the Au electrode.

What is the injection mechanism resulting in e-h recombination? Without a pn-junction for double injection, a front Schottky junction between the silicon and Au contact is used to inject the electrons into the superlattice structure and the deep depletion formed in the silicon substrate. The hot electrons produce eh-pairs in the deep depletion region of the substrate. The holes move up and are trapped in the superlattice region for recombination. [10,13]

Preliminary results from tight binding calculation gives the barrier height of 1eV between oxygen atoms and silicon on both sides. The measured value is only 0.5eV. Since measurements involve both height and width of the barrier, which is only one atomic distance, we consider the agreement is very fair.

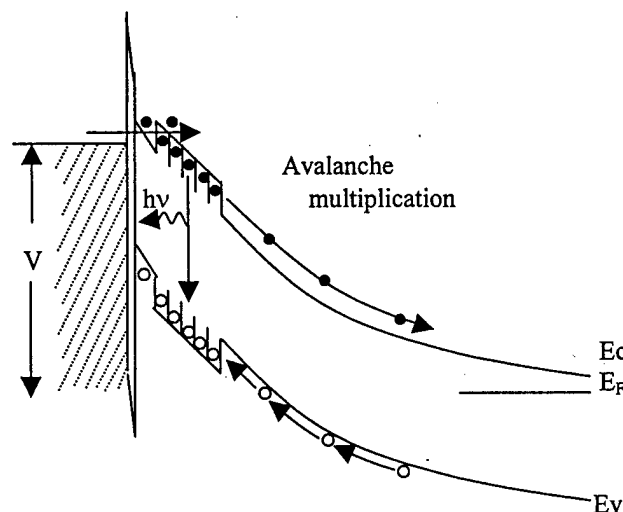


Fig.5 Band profile of the c-Si/O superlattice EL device under reverse bias. Electrons undergo avalanche multiplication providing holes for recombination with light emission.

Conclusions

The overall efficiency has been estimated to be somewhat higher than PSi. We know that PSi has an efficiency much below that of good semiconductor LEDs such as GaP. Remember silicon normally does not emit light at all. Besides all PSi can offer is leading researcher to look for other schemes with silicon. In this spirit, we are certainly stimulated by the first report of PL in the visible from PSi.[1]. Before we make a summary statement of our work, we like to point out that superlattices involving a-Si separated by oxides also work well.[14] However, a stable EL device is yet to be seen in this a-Si superlattice structure. It appears that the origin of light may very well be from the silicon oxygen complexes. Most of us are educated by the old schools that only bulk effects are worthy of note for any reliable

device. The art and technology of material science and fabrication techniques have come a long way in the recent decade. We can indeed control the interfaces. Therefore there is no reason why interfaces should be discarded from serious consideration for applications. In fact, as device size shrinks, interfaces may very well be the trend of the future devices!

REFERENCES

1. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046, (1990)
2. R. Tsu, *Nature* **364**,19, (1993)
3. R. Tsu, J. Morais and A. Bowhill, *Mat. Res. Soc. Symp. Proc.* **358**,825, (1995)
4. R. Tsu, A. Filios, C. Lofgren, J. Ding, Q. Zhang, J. Morais and C. G. Wang, ECS. 97- 11, Quantum Confinement: Nanoscale Materials, Devices and System", Edited by M. Cahay, J.P.Leburton, D.J.Lockwood, and S.Bandyopadhyay, *ECS Proc.* **97-11**,341, (1997)
5. J. Morais, Doctoral Thesis, UNICAMP, Department of Physics, Campinas, Brazil,1995, also J. Morais, Richard Lander, and R. Tsu, to be published.
6. R. Tsu, A. Filios,C. Lofgren, K.Dovidenko, and C.G.Wang, *Electrochem and Solid-State Lett.* **1**,80, (1998)
7. J.Ding and R. Tsu, *Appl. Phys. Lett.* **71**, 2124 (1997)
8. R. Tsu and L. Esaki, *Appl. Phys. Lett.* **22**,562(1973)
9. R. Tsu, Q.Zhang, and A.Filios, *SPIE* **3290**,246, (1998)
- 10..R. Tsu, A.Filios and Q.Zhang, "Perspectives of Light Emitters in Nanoscale Silicon", *Advances in Science and Technology 27, Techna Srl*, **55**(1999), also 9th CIMTEC, SX-Innovative Light Emitting Materials, Florence, Italy, 1998.
11. R. Tsu, K. Dovidenko and C. Lofgren, "A New Type of Superlattice: Semiconductor-Atomic Superlattice" *ECS Proc.* **99-22**, 295,(1999)
12. Q.Zhang, A.Filios, C.Lofgren and R. Tsu, "Ultra-stable Visible Electroluminescence from Crystalline Si/O Superlattice", *Physica E*, North-Holland, 1998.
13. R. Tsu, *ECS Proc.* **98-19**, 3(1999)
14. Z. H. Lu, D. J. Lockwood and J. -M. Barlbeau, *Nature* **378**,258, (1995)

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Recent Publications under ONR Grant:

1. R. Tsu, *Nature* **364**, 19, (1993)
2. R. Tsu, J. Morais and A. Bowhill, *Mat. Res. Soc. Symp. Proc.* **358**, 825, (1995)
3. R. Tsu, A. Filios, C. Lofgren, J. Ding, Q. Zhang, J. Morais and C. G. Wang, ECS. 97- 11, "Quantum Confinement: Nanoscale Materials, Devices and System", Edited by M. Cahay, J.P. Leburton, D.J. Lockwood, and S. Bandyopadhyay, *ECS Proc.* **97-11**, 341, (1997)
4. J. Morais, Doctoral Thesis, UNICAMP, Department of Physics, Campinas, Brazil, 1995, also J. Morais, Richard Lander, and R. Tsu, to be published.
5. R. Tsu, A. Filios, C. Lofgren, K. Dovidenko, and C.G. Wang, *Electrochem and Solid-State Lett.* **1**, 80, (1998)
6. J. Ding and R. Tsu, *Appl. Phys. Lett.* **71**, 2124 (1997)
7. R. Tsu, Q. Zhang, and A. Filios, *SPIE* **3290**, 246, (1998)

8. R. Tsu, A.Filios and Q.Zhang, "Perspectives of Light Emitters in Nanoscale Silicon", *Advances in Science and Technology 27, Techna Srl*, 55(1999), also 9th CIMTEC, SX-Innovative Light Emitting Materials, Florence, Italy, 1998.
- 9.R. Tsu, K. Dovidenko and C. Lofgren, "A New Type of Superlattice: Semiconductor-Atomic Superlattice" *ECS Proc.* 99-22, 295,(1999)
10. Q.Zhang, A.Filios, C.Lofgren and R. Tsu, "Ultra-stable Visible Electroluminescence from Crystalline Si/O Superlattice", *Physica E*, North-Holland, 1998.
11. R. Tsu, *ECS Proc.* 98-19, 3(1999)
12. R. Tsu, *Int. J. High Speed Electronics and Systems* 9 ,145(1998)

Invited talk

- R. Tsu, Q.Zhang, and A.Filios, *SPIE* 3290,246, (1998)
- R. Tsu, A.Filios and Q.Zhang, "Perspectives of Light Emitters in Nanoscale Silicon", *Advances in Science and Technology 27, Techna Srl*, 55(1999), also 9th CIMTEC, SX-Innovative Light Emitting Materials, Florence, Italy, 1998.
- R. Tsu, *ECS Proc.* 98-19, 3(1999)

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