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13. ABSTRACT (Maximum 200 words)

A new type of superlattices was introduced, consisting of a semiconductor such as silicon sandwiched between adsorbed oxygen atoms. This type of superlattices, compared to the heterojunction quantum structures, allow a wider variety of man-made solid because of tolerance to interfacial strain. Experimentally, Si/O superlattice is epitaxial with defect density below $10^9/cm^2$. A 9-period structure shows electroluminescence with a peak at 2.2eV, and an effective barrier height of > 0.5eV. Early on in this project, HRTEM has been exclusively used to demonstrate the epitaxy beyond the monolayer of oxygen introduced. A year ago, superlattice structure in the strain pattern demonstrated the extent of the interfacial strain, being ~ at least four lattice dimension. This is a very important finding because we may now use the SAS, Semiconductor-Atomic Superlattice as a matching section for the epitaxial growth of one with large strain onto the other. Some frequently asked questions : Do the oxygen atoms cover the entire 1x2 sites? If not, are there staggering present? Unfortunately the answers to these may require in-situ STM probing, which may be something for future considerations. Technologically, this research opens the door for future 3D ICs.

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*With several extensions with the last to allow payment for the refurbishment of the MBE system

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(1) List of Publications

Silicon Epitaxy on Si(100) with adsorbed Oxygen, R. Tsu, A. Filios, C. Lofgren, K.Dovidenko and C. G. Wang, Electrochem and Solid State Lett., **1** (2) 80 (1999).

Inverse Nottingham Effect Cooling, R. Tsu and R.F.Greene, Electrochem and Solid State Lett.**2**, 645 (1999)

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Phenomena in silicon nanostructure devices, R. Tsu, Appl. Phys. A **71** 391-402, (2000)
Cooling by Field Emission with Resonant Tunneling : Design Parameters, R. Tsu, Cold Cathod, ECS Proc. Vol. **2000-28**, 91 (2001)

Structure, Optical and Electronic Properties of Semiconductor-Atomic Superlattices, R. Tsu, J. C. Lofgren and O. Gurdal, Proc. 25th ICPS, Osaka 2000, Eds. N. Miura and T. Ando, (Springer-Verlag, Berlin Heidelberg 2001) p.1613

Structure of MBE Grown Semiconductor-Atomic Superlattices, R. Tsu and J.C.Lofgren, J. Crystal Growth, **227-228**, 21 (2001)

Heterogeneity in Hydrogenated Si : Intermediate ordered chainliuke objects, David V. Tsu, B.S.Chao, S.R.Ovshinsky, S.J.Jones, J.Yang, S.Guha, and R. Tsu, Phys. Rev. B**63**, 125338 (2001)

Transport through a nine period Si/O Suparlattice, Y-J Seo, J. C. Lofgren and R. Tsu, Appl. Phys. Lett. **79** 788 (2001)

Electronic and Optical Characteristics of Multilayer Nanocrystalline Silicon/Adsorbed Oxygen Suparlattice, Yong-Jin Seo, Raphael Tsu, Japan J. Appl. Phys. **40**, 4799(2001)

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Some Fundamental Issues for Heterojunctions – Multipole-electrode Hybrid Confinement, R.

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Challenges in the Implementation of Nanoelectronics, R. Tsu, in Special Issue of Microelectronics J. (Elsevier, 2003), LDSD-2002 Fortaleza, Brazil Dec. 8-13, 2002

Structure and Optoelectronic Properties of Si-O Superlattice, K. Dovidenko, J.C. Lofgren, F. de Freitas, Y.J.Seo and R. Tsu, Physica E: Low-dimensional Systems and Nanostructures, 2003

Quantum Devices with Multipole-Electrode – Heterojunctions Hybride Structures, R. Tsu Adv. Semicond. Heterostructures, Eds. M. Stroscio and M. Dutta, (World Sci. Singapore)

Cooling by Inverse Nottingham Effect with Resonant Tunneling , Y. Yu, R.F.Greene, and R. Tsu, Adv. Semicond. Heterostructures, Eds. M. Stroscio and M. Dutta, (World Sci. 2003, Singapore)

(2) Scientific personnel supported by this project and degrees awarded or pending:

Postdoctoral fellows

Dr. Q. Zhang Post-doctoral fellow, July 1998 – Dec.1998
Dr. Osman Gurdal : Post-doctoral fellow, Jan.2000 – June 2000 (1/4)

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A. Filios	PhD	July 1998 – May 1999,	(MS 1995, PhD 1999)
J.Dinkler	MS	July 1998 – May 1999,	(MS 1999)
Francisco B de Freitas	MS	July 1998 – Aug. 2000,	(MS 2000)
Franklin Bradley	MS	April 1 – Aug. 31, 2000,	went to industry
Armen Sevian	PhD	July 1999 – Aug. 1999,	went to industry, PhD expected in August 2003
Yuan Yu	MS	Aug. 2000 –Jan.31, 2003	(MS 2002)

(3) Reports of Inventions:

None at this time

(4) Accomplishments: Final Report on "A New Type of Silicon Superlattice: Hetero-Epilatttice" (Note that the word "Epilattice" coined by this PI did not catch on, so it was dropped! Now this type of superlattice is called SAS. See below)

Semiconductor-Atomic Superlattice (SAS)

Conventional superlattices are formed with repeating a basic period consisting of a heterojunction between two materials [1,2]. A new type of superlattice is formed by replacing the heterojunction between adjacent semiconductor layers by a monolayer of adsorbed species such as oxygen atoms; and

CO, molecules, etc.[3,4,5]. This new type of superlattice, SAS, semiconductor-atomic-superlattice, fabricated epitaxially, enriches the present class of heterojunction superlattices and quantum wells for quantum devices. The Si growth beyond the adsorbed monolayer of oxygen is epitaxial with fairly low defect density. At present, such a structure shows stable electroluminescence and insulating behavior, useful for optoelectronic and SOI (silicon-on-insulator) applications. In the case of polycrystalline silicon [6] and even amorphous silicon [7], sandwiched between a monolayer of oxygen forming superlattices, photoluminescence, (PL), in the visible has been reported. However stable electroluminescence is only observed with epitaxially grown Si/O superlattice.

Growth of Epitaxial Si-O Superlattice

After several failed attempts to realize the SLB (Superlattice Barrier) with thin silicon layers separated by thin oxides [3], a new method involving the exposure of oxygen followed by epitaxial growth of silicon using the in-situ RHEED (reflection high energy electron diffraction) for monitoring epitaxy, was introduced [4]. Figure 1 shows: (a) Si (100) with 1x1 and 1x2 RHEED diffraction. After oxygen exposure 20-50 Langmuir (1L is defined as an exposure of 100 seconds in 10^{-8} Torr), the 1X2 reconstruction is weaker but basically no change. This fact indicates that oxygen is physisorbed as O_2. After several atomic layers of Si deposition, the 1x2 reconstruction disappears, and 2D diffraction pattern becomes more as 3D as shown in (b). However, as shown in (c), the 1x2 diffraction pattern is fully restored after few more nm's of Si deposition. All oxygen exposure is at or under 100°C and Si MBE is at 575°C. Relatively low temperature is used for Si deposition to avoid possible oxygen diffusion. Recently we have obtained similar results at 650°C.

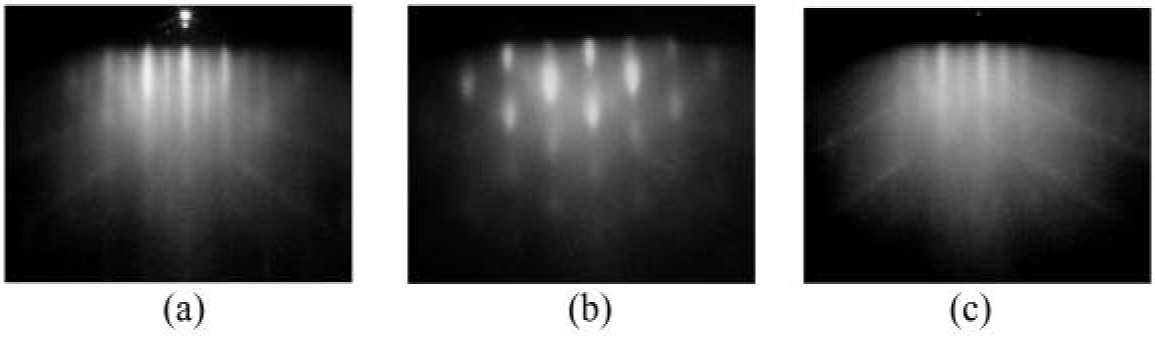


Fig. 1. RHEED of Si (100): (a) Buffer showing 1x1 and 1x2, (b) after oxygen exposure followed by Si deposition, and (c) restoration of reconstruction pattern of Si (100) after 3nm of Si growth

The high resolution cross-section TEM of a sample with Si (buffer) / (O-Si (1.1nm)-O-Si (1.1nm)-O) / Si on Si(100) is shown in Fig.2-left. The "whitish" part of the figure may indicate where the oxygen cluster is located. Epitaxy is continued beyond this "whitish" region. We have also succeeded the SAS with Si (111). The structure is slightly more defective than Si (100). Although we have relatively continuous layer of oxygen, as pointed out before [8], discontinued clusters can serve as a barrier because electrons, as de Broglie waves, cannot pass through region of space smaller than the wavelength. This is a good place to emphasize that there are two mechanisms – step in energy, and/or step in geometrical shape both give rise to an effective barrier for electrons. In Fig.2-right, plane view TEM shows rather low defect densities, below $10^9/cm^2$.

We have lowered the defects by almost two orders of magnitude during the past couple of years. Thus we are optimistic that further reduction should be possible. Note that the defect density in Si-Si dioxide interface for most MOS gates is generally much higher.

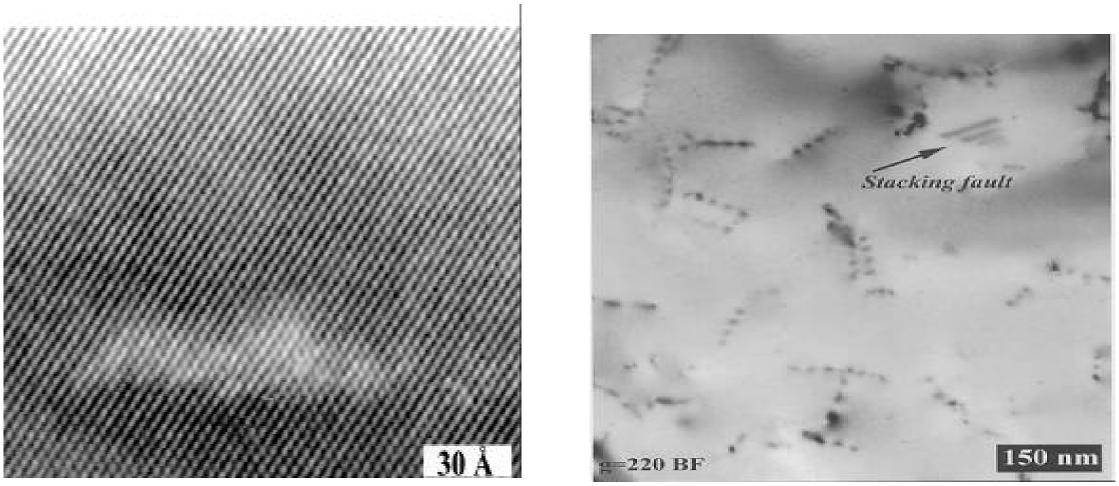
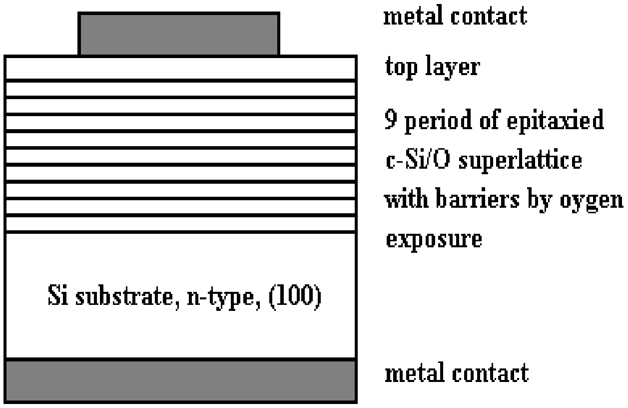


Fig.2. High resolution cross-section TEM on Si(100), left. From bottom of figure towards the top showing Si (buffer) / (O-Si (2.2nm)-O) / Si epitaxy. Plane-view TEM of the sample, right. The defect densities is below $10^9/cm^2$.

As pointed out previously [9], if oxygen leak valve is left on during the silicon deposition, horrendous amount of defects are generated, although the 3-D diffraction pattern still persists. Therefore our results are similar to what is generally known that it is impossible to grow good Si epitaxially on an oxide layer.

Electroluminescence Diode (ELD)

Figure 3-left shows a schematic of a 9-period EL device with a Si/O superlattice as the active layer. EL from the top through a partially transparent Au electrode of dimension 0.5x1.2mm is shown on the right figure. EL covers the whole contact with bright EL around the edges. The dark spot is due to the wire contact The voltage applied across the Schottky diode is between –20V reverse-bias to as low as –6.8V reverse-bias. This point will be discussed more fully when the life-test result is shown. Annealing in H_2 + N_2 (1:10) at 420°C for 10 min leads to higher EL intensity.



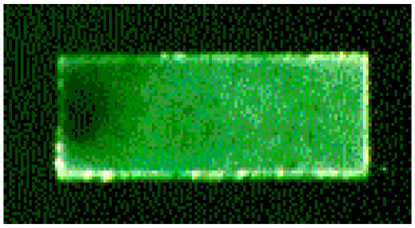


Fig.3. The left figure shows a schematic of the EL device with a 9-period Si/O superlattice as the active layer. EL from the top through a partially transparent Au electrode of dimension 0.5x1.2mm is shown on the right figure. The dark spot is due to the wire contact

Figure 4 shows a typical EL and PL. Although the main peak is located at 2eV, the emitted light appears greenish because the EL spectrum extends to photon energy beyond 3.5eV. The cutoff due to the laser line is evident in the PL spectrum. Of course it is also possible that the broad spectrum reflects the presence of Si – O complexes. However the strong shoulder extending beyond 3.5eV is most likely due to the complex. Figure 5 shows one of our life-test the EL device is obvious. In fact, we have also performed under constant current after the first 30 days, the applied bias drops down to – 6.8V. The longest operating time is over 1 year. The applied bias includes the voltage drop over the substrate. The drop from – 10.4V to – 6.8V is probably due to annealing effects. After the initial 30 days of operation, there is observed an increase of 50% in the light output [9].

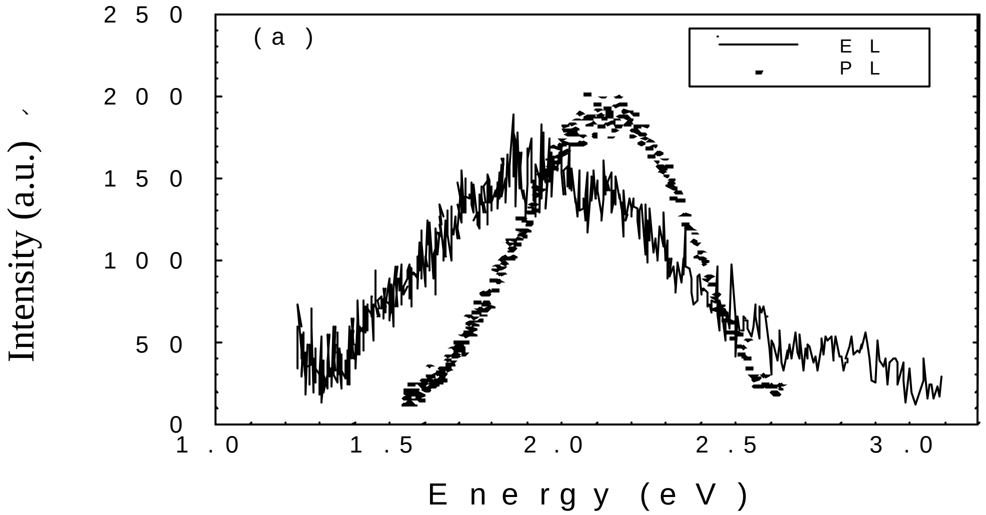


Fig. 4. PL and EL of a typical Schottky diode with 9-period of Si-O superlattice.
The 457.9 nm line of the argon laser was used for the PL spectra.

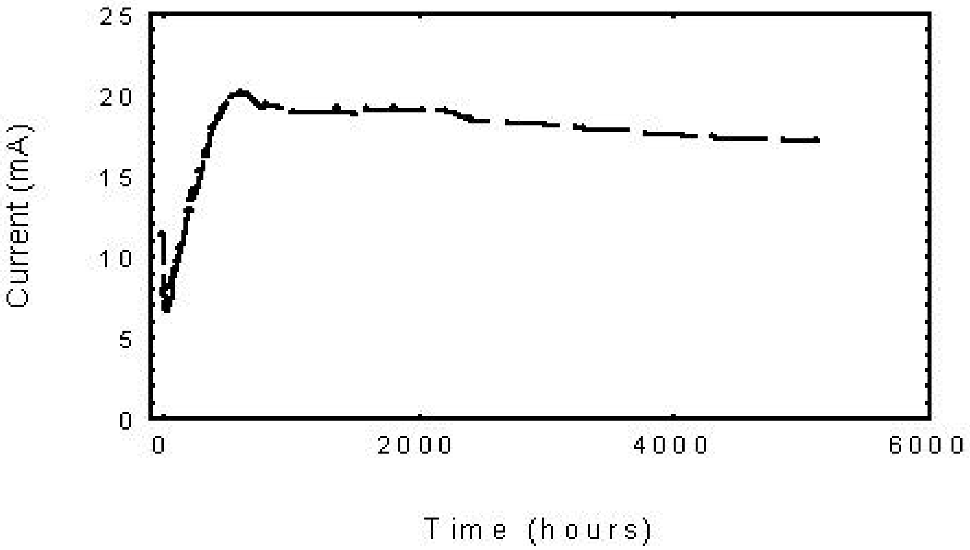


Fig. 5. Current versus time under reverse bias, -10.4V to – 6.8V

The LUMO and HOMO, L and H, are obtained from the coupling of $^3P_{2,1,0}$ of the atomic Si at –8eV (8eV below the vacuum), and the first excited state of the atomic oxygen, $^5S_0$ at –4.3eV, using the coupling constant α_o. Table I summarizes the calculated ΔE_c and ΔE_v versus α / α_o using $\alpha_o = 5.11$eV giving ΔE_c = 3.2eV adjusted to fit the Si/SiO$_2$ case. (a-SiO$_2$ / Si has a barrier height of 3.2eV). Note that for our structure, our model consists of equal number of oxygen and silicon atoms, resulting in $\alpha / \alpha_o = 0.5$, shown in bold. Therefore the sharp peak in Fig. 6 is very close to the Si-O complex represented by the position of the LUMO state.

α / α_o (eV)	1.0	0.75	0.5	0.25
LUMO (eV)	-0.7	-1.58	**-2.98**	-3.9
HOMO(eV)	-11.6	-10.37	**-9.27**	-8.35
ΔE_c (eV)	3.2	2.32	**0.92**	0
ΔE_v (eV)	6.55	5.37	**4.27**	3.35

Table I Calculated ΔE_c and ΔE_v vs α / α_o using $\alpha_o = 5.11$eV, $\alpha / \alpha_o = 0.5$ applies to SiO.

Barrier Height of O-Si (1.1nm)-O on Silicon

The barrier height of several two-period structures have been measured.[10,11] Figure 6, from Ref. 11 shows the measured barrier height of 0.5eV. The calculated value is 0.92 eV, which is close. However, in transport measurements, because of the involvement of both the barrier height and barrier width, usually the determined value using an activated process is lower.

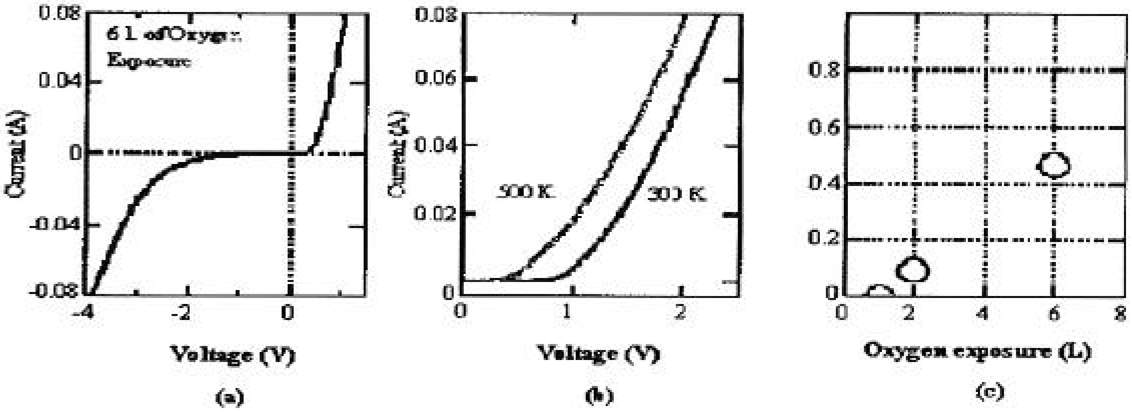


Fig. 6. (a) Current vs. Voltage of a superlattice barrier with 6L oxygen exposure having a Si (1.1nm) layer in between two adsorbed oxygen. (b) Temperature dependent I-V, and (c) Barrier height E_b vs oxygen exposure in L (Langmuir).

Possible models of Si-O superlattice

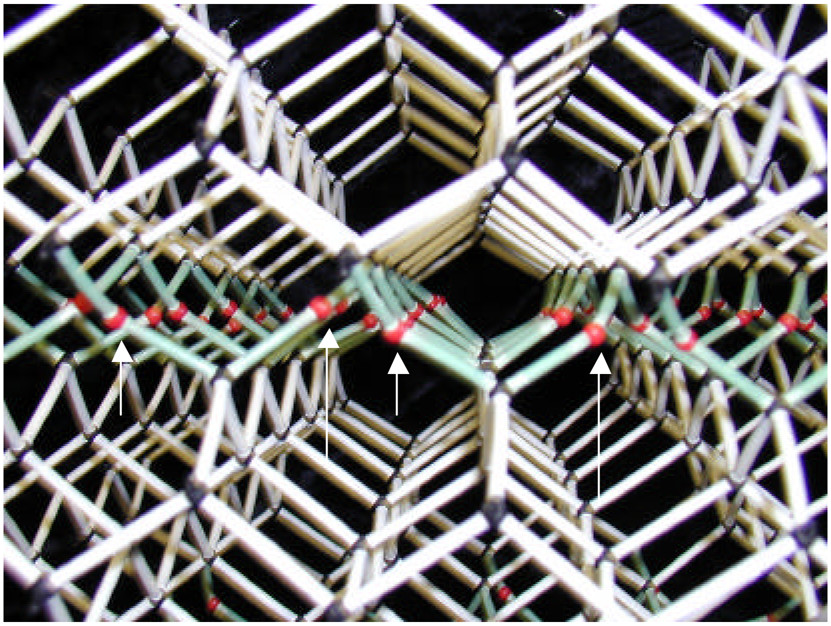


Fig. 7. A hand-built model with a single layer of oxygen. The arrows point to the rows of oxygen atoms.

A hand-built model with a single layer of oxygen atoms is shown in Fig. 7 . This model is based on the following : A Si atom at (000) is replaced by two oxygen atoms, one at **-J** and a second one at **J,** resulting in the two oxygen atoms at (-J00) and (J00). The oxygen at (-J00) is bonded to (-11δ) and (-1-1-δ) silicon atoms. Similarly the oxygen at (J00) is bonded to (1-1δ) and (11-δ) silicon atoms. Preliminary calculation [12] using J = bond length of Si-O, the distance $\delta = \mathbf{a}/8$, with **a** being the lattice constant of Si. The maximum strain is 6.4% based on $\Delta\theta/\theta$ from the hand-built model using $\delta = \mathbf{a}/8$. However, using Density Functional Calculation [13], δ is allowed to vary, the strain is lowered to 1%. There are at least two other possible models: (a) monolayers of oxygen separated by a monolayer of Si, and (b) monolayer of oxygen forming a reflection symmetry for the Si above the oxygen plane and Si below the plane. Presently, these two are being examined in detail.

OBSERVATION OF STRAIN PATTERN IN Si/O Superlattice

Because strain penetrations [14] from the monolayer of oxygen atoms into adjacent silicon layers, whenever the superlattice period is such that the period exceeds the penetration depth, the strain pattern shows up in the TEM. [15] As shown in Fig.8, with $N_{Si} > 2\delta$, the number of silicon layers between two oxygen monolayers given by $N_{Si} \sim 32$, and the number of penetration layers from the oxygen monolayer $\delta \sim 6$, the strain pattern shows up. While before, with $N_{Si} \sim 8$ in the 9 period Si/O superlatices, no strain pattern was observed in TEM. An enlarged picture in Fig. 9 clearly shows the extent of the strain.

Fig.8 A Superlattice structure showing the period of the silicon and monolayer of oxygen.

Strain (shown in ||||||||||||) extends ± 6 atoms from the O monolayer

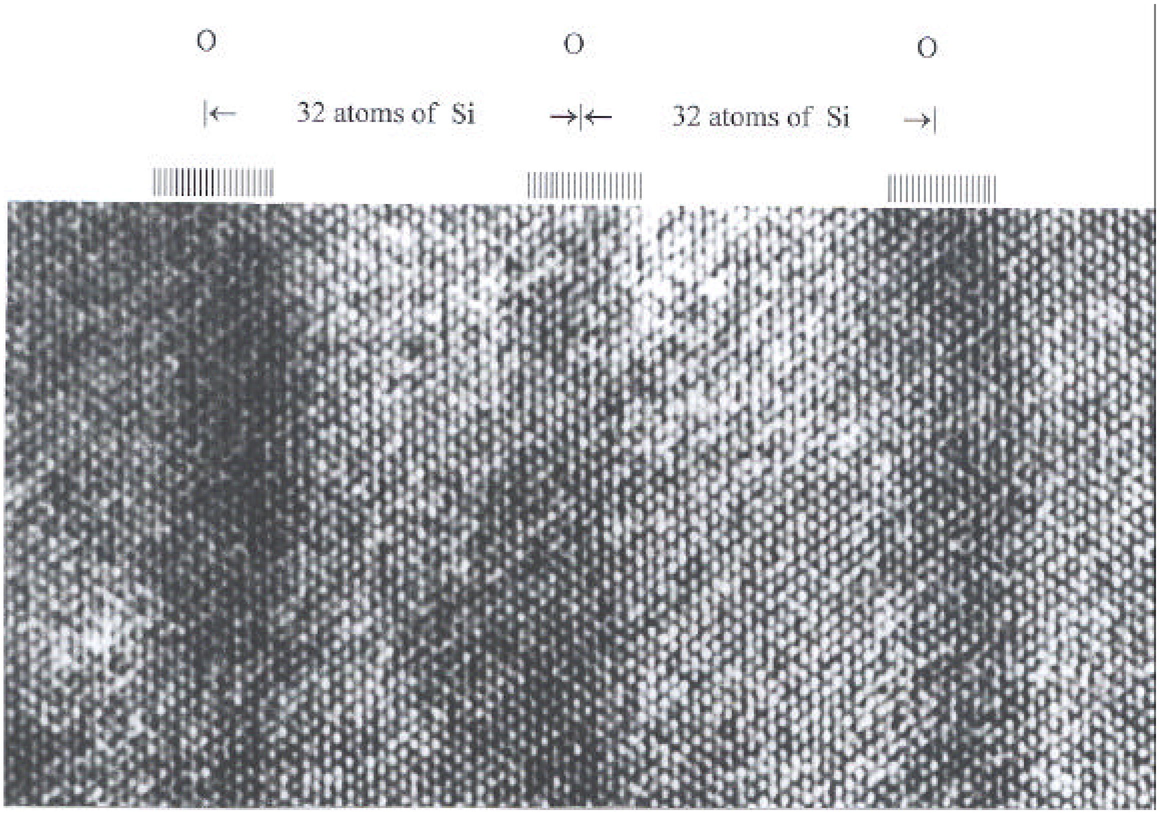


Fig. 9 Strain Pattern in Si/O Superlattice

Current – Voltage of a 9-period Si/O superlattice

I-V of a 9-period [16], is shown in Fig.10 taken from Ref.14, after annealing in H_2 and O_2 , where blocking is clearly shown. A sufficiently thick Si/O superlattice, for example, 20-30nm thick, should provide insulation to replace the usual SOI. Therefore, the biggest application of the Si/O superlattice may be a step toward the fabrication of 3D ICs.

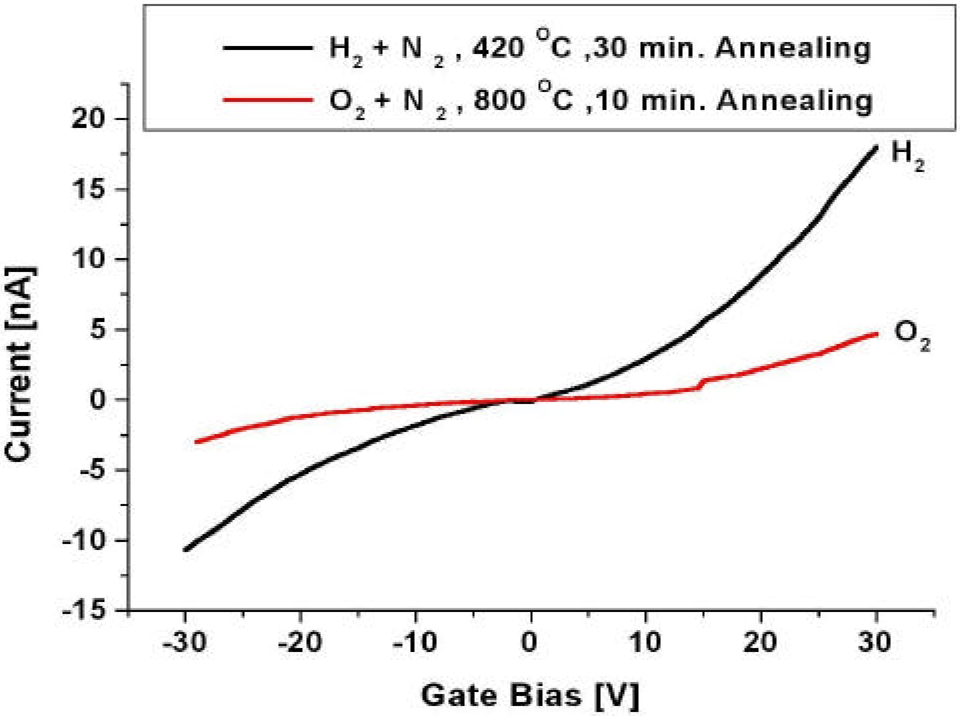


Fig. 10. Typical I-V of a nine period Si/O superlattice after two annealing conditions.

Conclusion

In conclusion, Si/O superlattice is a reality. The structure is epitaxy with low defect density. The defects are mostly stacking faults and dislocations. Preliminary modeling indicates that there are at least three possible ways for the monolayer of oxygen in a crystalline silicon matrix. One of these is shown in more detail while the other two are just mentioned. The estimated strain is below 1%. Visible and near UV light are observed in PL and EL. They are believed to originate both from quantum confined silicon as well as from Si/O interfacial regions. Life-test of several ELD devices shows stable continuous operation for over one year. However, this work may form the basis of a silicon based optoelectronic chip, as well as possible 3DICs.[17]

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