Project II. 1

NANOSTRUCTURES FOR NANOELECTRONICS AND PHOTONICS

Project leader: A. G. Nassiopoulou

Key researchers: A. G. Nassiopoulou, E. Tsoi, S. Gardelis and N. Papanikolaou

Phd students: M. Kokonou, A. Olziersky, A. Salonidou, A. Zoy, V. Gianneta

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- EU IST NoE SINANO, 1/1/2004-31/12/2006, Contract N°: 506844
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- EU IST I_3 ANNA, 1/12/2006 – 1/12/2010, Contract N°:026134

Research orientation:

- Semiconductor (Si, Ge) nanostructures: Growth by LPCVD and sputtering, characterization: electrical, optical, structural
- Si/Ge nanocrystal non-volatile memories
- Ultra-thin porous alumina template technology on silicon. Application in through-pore silicon nanostructuring
- Self-assembly of quantum dots on nanostructured surfaces
- Theory (Ballistic transport in nanostructures, Surface plasmons in thin metallic films, classical molecular dynamics and nanoscale heat transport)

The activity on semiconductor nanostructures started at IMEL at the early nineties and it was conducted within different EU projects, in collaboration with other European groups (Esprit-EOLIS, IST FET SMILE No 28741, IST FORUM FIB No 29573, IST NoE SINANO etc). Worldwide original results were produced, including fabrication of light emitting silicon nanopillars by lithography and anisotropic etching and investigation of their properties, growth of Si nanocrystal superlattices by LPCVD and high temperature oxidation/annealing with interesting optical properties, fabrication and characterization of LEDs based on Si nanopillars, nanodots and others.

The present focus of research is on self-assembly and ordering of Si and Ge quantum dots on nanostructured silicon surfaces and their application in nanocrystal memories and photonics. For Si nanostructuring, a non-lithographic process using porous alumina template technology has been developed. Porous alumina ultra-thin films are grown on silicon by electrochemistry. By appropriately choosing the electrochemical conditions used, pore size and density are monitored. Through-pore silicon nanostucturing follows the pore size and density. Arrays of SiO2 nanodots on Si were fabricated and characterized. Dot size varies from few nm up to few hundreds of nm.

Another technology under development is the growth of ultra thin porous silicon films by electrochemical dissolution of silicon in the transition regime between porosification and electropolishing. Under appropriate conditions, the obtained films are amorphous with embedded Si nanocrystals of various sizes. Under other conditions, the films are nanocrystalline.

Characterization of nanostructures includes investigation of their optical, electrical and structural properties.

The theoretical group focuses on the investigation of ballistic transport in nanostructures, surface plasmons in thin metallic films, classical molecular dynamics and nanoscale heat transport.

A brief overview of the main results obtained in 2006 is given below.

RESEARCH RESULTS

A. LPCVD growth of double-layers of silicon nanocrystals within the gate dielectric of a MOS structure for improved non-volatility in nanocrystal memories

A Salonidou and A. G. Nassiopoulou
In collaboration with K. Giannakopoulos and A. Travlos from the Institute of Materials Science for TEM work

Layers of silicon nanocrystals embedded in SiO_2 are fabricated in this work by low-pressure chemical vapor deposition (LPCVD) of amorphous Si, followed by high temperature thermal oxidation and annealing. The thickness of the amorphous layer as well as the oxidation time are adjusted so as to get the desired thickness of the nanocrystal layer and the top oxide. The main advantage of this process are the tunability of nanocrystal size and the good quality of barrier silicon oxide.

By using the above process, single and double layers of silicon nanocrystals were fabricated within the gate dielectric of a MOS memory structure.

By using doubly-stacked dots layers (fig. II 1.1 a,b), with a smaller dot with diameter below ≈3nm underneath a larger one, of size ~5nm, it is possible to create a barrier to carriers from the dot to the silicon substrate, as indicated schematically in fig. 7a. This structure is expected to improve data retention in the low voltage regime due to the band offset between the two dots, induced by more pronounced quantum-confinement bandgap opening in the smaller dot compared to the larger one, as shown schematically in fig II.1.1c.

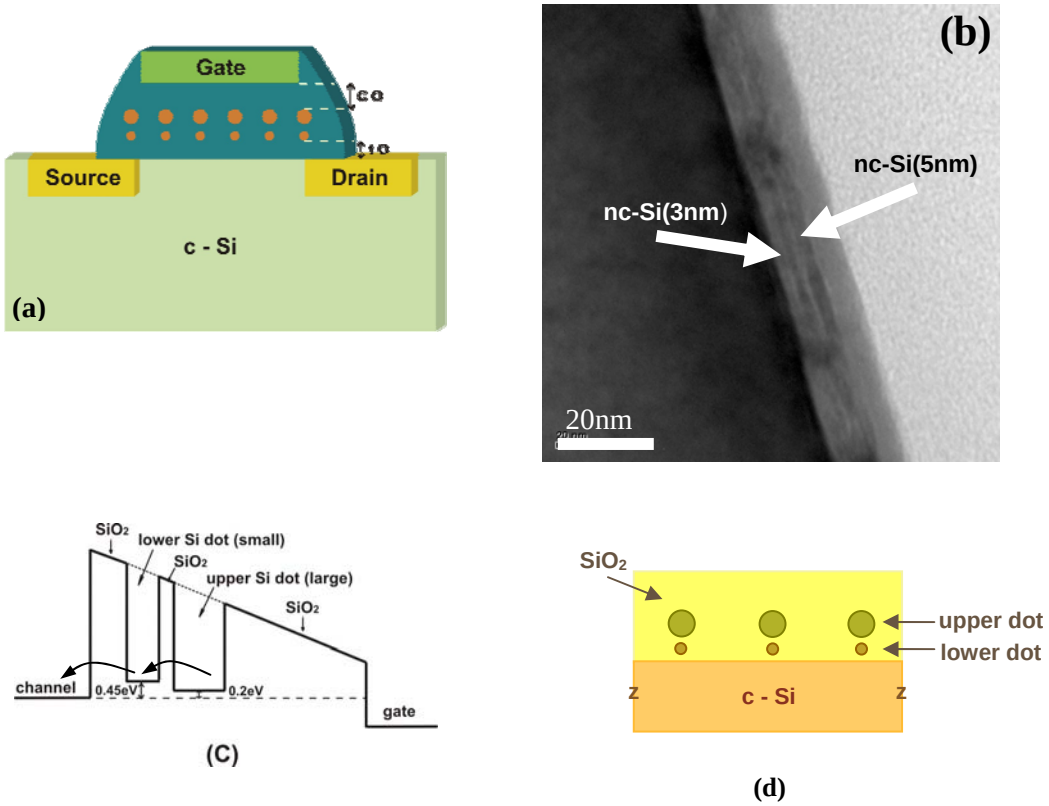
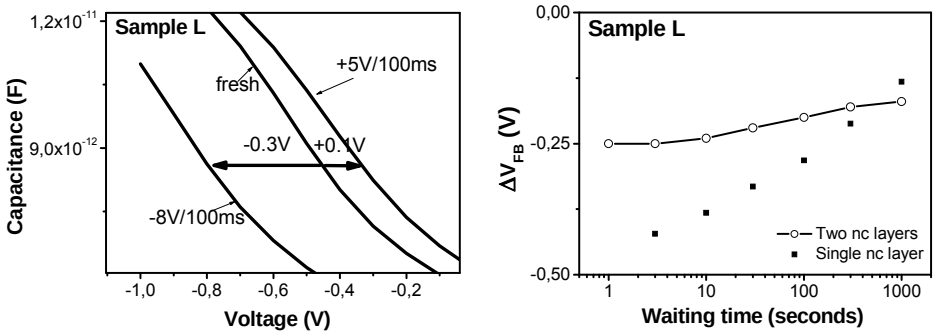


Fig. II.1.1:

A sample structure as in fig. II.1.1b was used to fabricate nanocrystal MOS capacitors that have been characterized for their charging properties by electrical measurements. Double-dot-layer structures showed much slower charge loss at zero bias compared with similar structures with a single nanocrystal layer. This is illustrated in fig. II.1.2. In (a) we see the shift in C-V curves after application of a positive (+5V/100ms) or negative (-8V/100ms) pulse on the gate of a device with the following gate dielectric structure on p-type silicon: tunnel oxide 3.5nm/NC_1-d=3nm/inter-dielectric:1.5nm/NC_2-d=5nm/control oxide:8nm. The retention characteristics (ΔV_{FB} versus time) after writing at -8V/100ms are shown in fig. II.1.2B (open circles). In the same graph we show in full squares the retention characteristic of a similar single-dot-layer device with nanocrystal size d=3nm. In this second case, under the same charging conditions the maximum shift in V_{FB} is larger, but charge loss is much faster.



(a) (b)

Fig. II.1.2:

B. Growth of ultra-thin anodic Si films for optoelectronic and nanoelectronic applications

S. Gardelis and A.G. Nassiopoulou

We developed a method for fabricating ultra-thin (18-80 nm) light emitting films with embedded silicon nanocrystals by anodization of bulk crystalline Si in the transition regime between porocification and electropolishing using short mono-pulses of anodization current. The size of the nanocrystals decreased with increasing current density and it was in the range of 3-7 nm with current densities in the range of 130-390 mA/cm^2. At the highest current densities used the film/substrate interface was very sharp (Figure a), while at lower current densities the interface contained nanostructured silicon spikes protruding from the substrate into the nanostructured film. All the investigated films exhibited broad photoluminescence at room temperature at around 630 nm (Figure b). The photoluminescence intensity increased considerably with increasing anodic current density in the transition regime (up to 100 times in the films we studied), whereas thickness of the corresponding films increased by only three times. We attributted the effect of intense light emission to quantum confinement in the smaller Si nanocrystals embedded in these films (smaller than 2nm). The growth of such films is investigated due to their potential use in optolectronic and nanoelectronic applications.

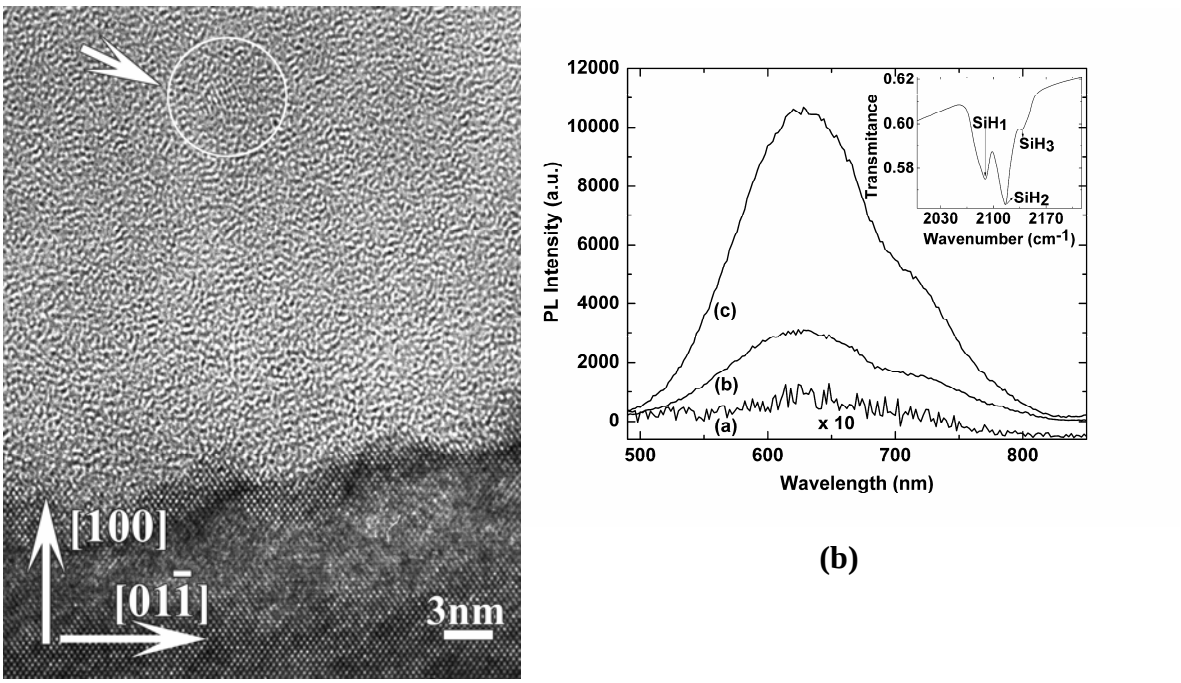


Fig. II.1.3: (a) *HREM image obtained from the film grown at the highest current density used, showing a smooth interface and Si nanocrystals embedded in an amorphous matrix.* ***(b)*** *Photoluminescence obtained from the films at room temperature . The inset depicts FTIR spectrum obtained from the films, showing the presence of Si-H_x vibrational modes at the film surfaces.*

C. Ultrafast transient photoinduced absorption in silicon nanocrystals: Coupling of oxygen-related states to quantized sublevels

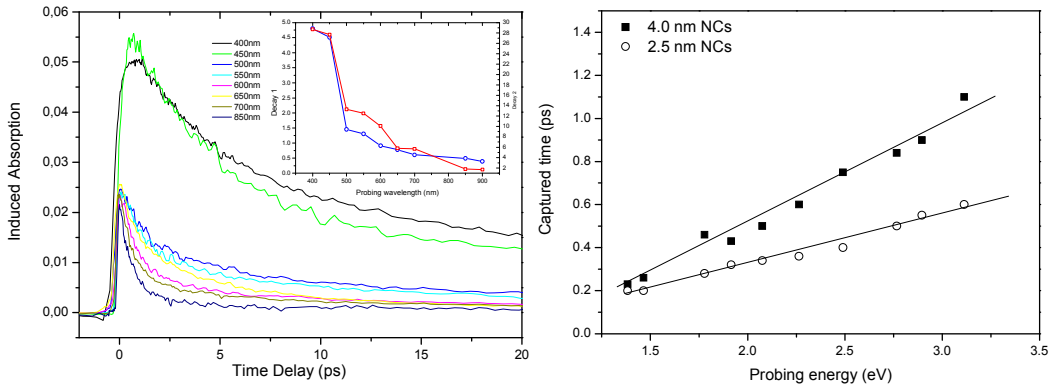
Emmanouil Lioudakis[1], A. Othonos[1], A. G. Nassiopoulou

[1] Collaborators from the University of Cyprus

We have studied transient photoinduced absorption (TPA) in single monolayers of oxidized Si-NCs embedded in amorphous SiO_2 matrix with two different NC sizes (2.5 and 4nm). The experimental TPA measurements along with optical absorption measurements reveal that the light-absorption process takes place inside the Si-NC band structure, suggesting that the photoexcited carriers are in oxygen-related states. From our experimental results, we observe two different relaxation mechanisms/channels for the free carriers at the first few picoseconds before radiative recombination (PL). Probing at different energy states, we suggest that for both NC sizes the fast relaxation mechanism corresponds to the internal relaxation of oxygen-related states at the interface of Si-NCs with SiO_2. The slower relaxation process may be correlated with quantized sublevels which are formed due to the embedded NCs in the SiO_2 matrix.

As an example, in fig. II.1.4a, we present the experimental data of TPA of the larger Si-NCs (4 nm) following optical excitation around the oxygen-related states (400 nm) at different probing wavelengths ranging from 400 to 900 nm. These data were obtained from the combination of the temporal reflectivity and transmittance changes of the sample. After the excitation the photogenerated carriers populate the electron/hole oxygen-related states. As the carriers relax a coupling to higher energy states (induced absorption) is achieved due to the probing pulse. Due to the strong correlation of the oxygen-related states of these materials, effects at lower energy states such as state filling do not appear in our measurements. The initial fast rise of experimental results corresponds to the effective time [$\tau_0(\lambda)$] until an efficient coupling has been achieved. This time is a basic characteristic for each material and is directly related to the initial carrier density as well as the opened optical channels at the particular energy difference (probing energy resonance). In fig. II.1.4b, we

present this effective time as a function of the probing energy. As seen from these results, the time increases linearly with the probing energy. This means that with increasing probing energy, the coupling has been achieved at longer times. The latter is attributed to the reduced wave function overlapping between the coupled energy states.



(a) (b)

Fig. II.1.4: *(a) (Color) Ultrafast TPA measurements from 4 nm Si-NCs at different probing wavelengths. The inset shows both fast and slow relaxation times as a function of probing wavelength (400-900 nm). (b) Effective time as a function of the probing energy for both Si-NC sizes. The lines are the linear fits in the experimental data.*

D. Fabrication of SiO_2 quantum dots on Si substrates through thin films of porous alumina. Their use in Si nanopatterning

V. Gianneta, M. Kokonou and A. G. Nassiopoulou

SiO_2 nanostructures on silicon substrates are attracting interest because they exhibit very useful properties for various applications in nanoelectromechanical systems (NEMS) and nanoelectronic devices. Nanostructuring of silicon through the pores of anodic alumina is a promising technique due to the low cost and the simplicity of the whole experimental procedure.

In this work, regular arrays of SiO_2 quantum dots were fabricated on silicon through alumina pores. Porous alumina thin film on Si constitute a very interesting material fabricated by anodization of Al films under certain electrochemical conditions that lead to self-organization of the film and formation of regular vertical pores arranged in an hexagonal close-packed structure. The SiO_2 dots start to form during anodization after total aluminum consumption, when the electrolyte reaches the Si substrate. The size and density of the quantum dots depend strongly on the electrochemical conditions applied and the structural characteristics of the porous alumina layer.

The SiO_2 dots are homogenous in diameter and height and their arrangement follows the initial hexagonal structure of the porous alumina layer.
We fabricated arrays of dots with size that varied from 2-10 nm in height and 10-30 nm in diameter.

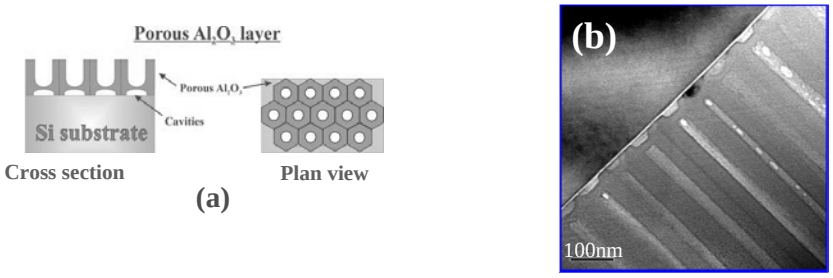


Fig. II.1.5: *(a) Schematic representation of a cross section and a plan view of porous alumina thin film on Si. (b) TEM image of porous alumina thin film (cross section) on Si*

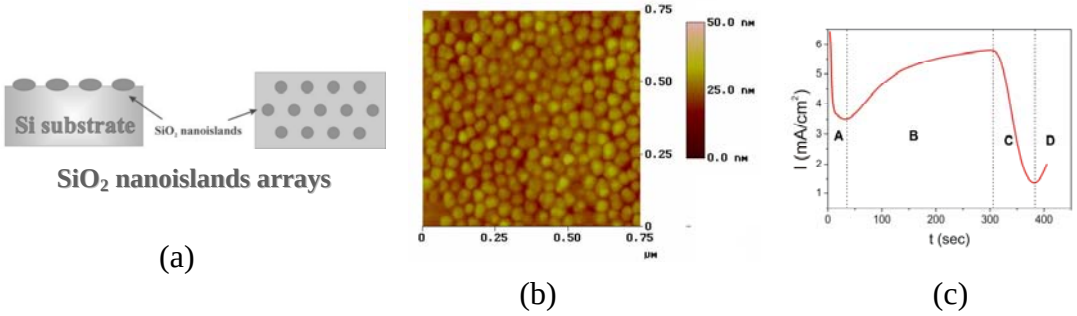


Fig. II.1.6: *(a) Schematic representation of SiO_2 dots on Si (cross section and plan view). (b) AFM image of an array of such dots on Si. (c)Example of anodization curve.*

By removing the SiO_2 dots, we obtain a nanopatterned Si surface (bare or oxidized), which is appropriate for self-assembly of nanodispersed Si or Ge quantum dots.

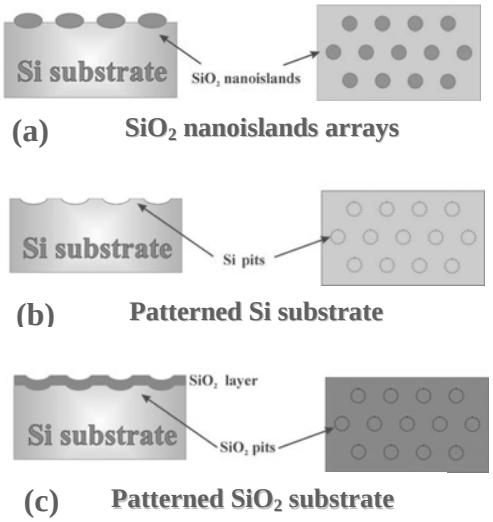


Fig. II.1.7: *Successive steps for Si nanopatterning. (a) Arrays of SiO_2 dots fabricated through porous anodic alumina. (b) Nanopatterned bare Si surface after removal of the dots. (c) Nanopatterned oxidized Si surface (oxidation of the nanopatterned surface shown in (b))*

E. Self assembly of gold nanoparticles by dielectrophoresis

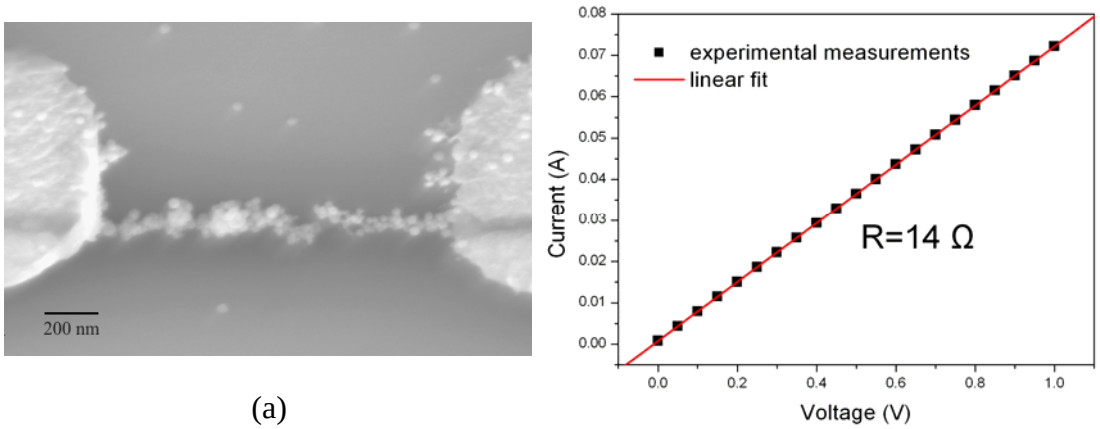
A. Zoy and A.G. Nassiopoulou

In this work we developed the dielectrophoresis technique for controllable and rapid assembly of Au nanostructures between electrodes. This technique is based on the force exerted on the induced dipole moment of a dielectric or conductive particle by a non-uniform electric field. Alternative (AC) electric fields are often preferred in order to suppress electrochemical reactions, as for example electrolysis at the electrodes surface and to overcome the limitation of strong surface particle charge. DEP is suitable for microfluidic applications and nanoassembly.

At IMEL, dielectrophoresis has been used for the controllable assembly of gold nanoparticles between electrodes and the formation of conductive nanowires with micrometer length. Different aqueous colloidal gold nanoparticles with average diameter of 20, 30, 40 and 45 nm were assembled between gold or platinum electrodes with 1 μm distance between them

placed on a 150 nm thick SiO_2 layer. The effect of the frequency and strength of the applied field on the particle accumulation process was investigated. Two typical results at low and higher frequency including SEM images and corresponding current-voltage characteristics are shown in fig.II.1.8.

At low frequencies, the Au nanoparticles are aggregating and the corresponding I-V characteristic is polynomial, which is indicative of space charge limited conductivity of the structure. At higher frequencies, the Au nanoparticles are deposited in a discrete way as shown in fig. II.1.8(a). In this case, samples exhibit linear conductivity with the applied voltage. An example is given in fig. II.1.8b. In this case the transport mechanism is hopping conductivity.



(a) (b)

Fig. II.1.8: *SEM image of a single Au nanoparticle chain formed by dielectrophoresis between micron-distant electrodes, with V-groove lines between the electrodes. The applied ac electric field had an amplitude of 3 V at 2 kHz. In (b) we see an example of current-voltage characteristic of the nanoparticle chain and the corresponding linear fit from which a chain resistance of 14 Ω is deduced.*

F. Ballistic transport in nanostructures

N. Papanikolaou

As modern electronic devices are getting close to 10 nm in dimensions there is a growing interest in alternative technologies which will replace Si. Understanding electronic transport in the atomic scale is an important milestone towards this goal. We have investigated theoretically the ballistic electronic conductance through single atoms attached to Cu and Pd crystalline electrodes. We use state of the art *ab initio* electronic structure methods based on density functional theory. We have systematically studied different contacts and different leads. One important conclusion is that the conductance of the system is mainly determined by the electronic properties of the atom bridging the leads. The contact geometry is crucial only when transition metal atoms are present in the contact. Our calculations offer a transparent physical picture in accordance with recent experimental reports.

f_1 Surface plasmons in thin metallic films

Surface plasmon excitation is responsible for many interesting phenomena in optics like extraordinary transmission through metal films with sub-wavelength hole arrays, surface enhanced Raman scattering and negative refraction. There are also interesting potential applications in building optical filters and sensors as well as subwavelength optical waveguides. We study surface plasmons in thin films decorated with metallic sphere arrays. We focus on the interaction between flat surface plasmon- polaritons and particle plasmons. Maxwell's equations are solved exactly using a multiple scattering formalism which combines

high accuracy with efficiency. Light transmission through such structures can be enhanced by an order of magnitude.

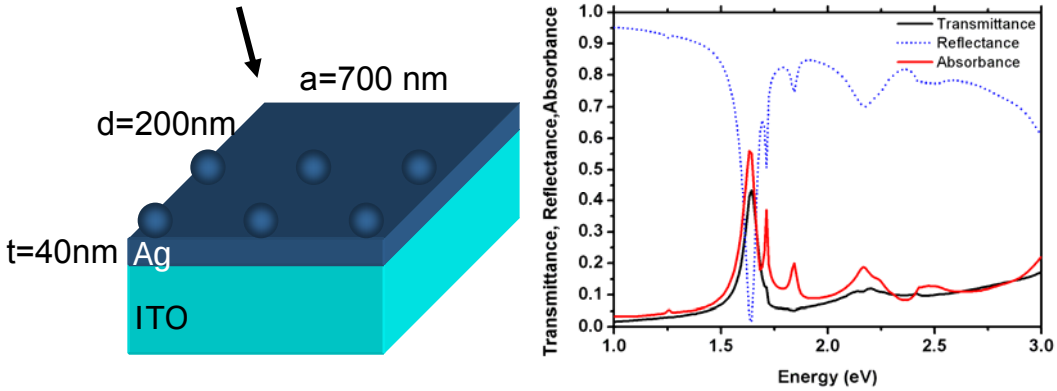


Fig. II.1.9: *Left panel: Schematics of a square array of metallic spheres (diameter 200nm, lattice constant 700 nm) on a 40 nm thin Ag metallic film on top of indium tin oxide (ITO) substrate. Right panel: Transmission, Reflection and absorption through the system depicted on the left. For photon energy close to 1.6 eV, transmittance is almost 45%.*

In the system shown in the figure the presence of the sphere array increases the transparency of the film by a factor 10 compared with the system without the spheres. Similar results have been reported before in systems with periodic arrays of particles on both sides of the film, and where confirmed experimentally. The presence of a high refractive index dielectric like ITO in this case allows the leakage of light without the need of periodic structures on both sides of the film. Our aim is to use these results in the design of new, highly sensitive, optical sensors.

f_2 Classical molecular dynamics and nanoscale heat transport

We have developed a new classical molecular dynamics computer code appropriate for semiconductor materials. Our implementation includes an energy minimizer and the molecular dynamics. We have implemented several classical potential parameterisations like, Stilliger-Weber, Tersoff, EDIP, for Si, Ge, and C, embedded atom method potentials to use in metallic systems as well as metal semiconductor interfaces. A few silicon dioxide potentials are also available.

Provided the potential is available, the method can be used for a variety of problems like calculation of local pressure and tension in nanostructures, diffusion, oxidation, growth etc. We have first applied the method in the calculation of the thermal conductivity of SiC nanowires. We use a non equilibrium molecular dynamics method by creating a heat flux along the nanowire, and calculating the resulting temperature gradient. Our results show that thermal conductivity is greatly reduced compared to the bulk SiC which is mainly due to scattering at the nanowire surface.

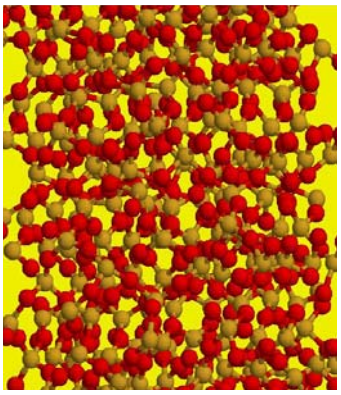


Fig. II.1.10:
Amorphous SiO2 snapshop from MD simulation

PROJECT OUTPUT in 2006

Publications in Refereed Journals

1. “Photoluminescence lifetimes of Si quantum dots”, Xanthi Zianni and A. G. Nassiopoulou, J. Appl. Phys. 100, 074312 (2006)
2. “Growth and characterization of high density stoichiometric SiO2 dot arrays on Si through anodic porous alumina template”, M. Kokonou, A. G. Nassiopoulou, K. P. Giannakopoulou, A. Travlos, T. Stoica and S. Kennou, Nanotechnology 17, 2146 (2006)
3. “Probing carrier dynamics in implanted and annealed polycrystalline silicon thin films using white light”, E. Lioudakis, A. Othonos and A. G. Nassiopoulou, Appl. Phys. Lett. 88 (18) 181107 (2006)
4. “Femtosecond carrier dynamics in implanted and highly annealed polycrystalline silicon”, E. Lioudakis, A. G. Nassiopoulou, A. Othonos, Semicond. Sci. & Techn. 21 (8), pp. 1041-1046 (2006)
5. “Ellipsometric analysis of ion-implanted polycrystalline silicon films before and after annealing”, E. Lioudakis, A. G. Nassiopoulou and A. Othonos, Thin Solid Films 496 (2), pp. 253-258 (2006)
6. “Ge quantum dot memory structure with laterally ordered highly dense arrays of Ge dots”, A. G. Nassiopoulou, A. Olzierski, E. Tsoi, I. Berbezier and A. Karmous, J. Nanosci. Nanotechnol., vol. 7, 316-321, 2007 (on line 2006)
7. “Two-silicon-nanocrystal layer memory structure with improved retention characteristics”, A. G. Nassiopoulou and A. Salonidou, J. Nanosci. Nanotechnol., vol. 7, 368-373, 2007 (on line 2006)
8. “Ab initio approach to the ballistic transport through single atoms”, A. Bagrets, N. Papanikolaou, and I. Mertig, Phys. Rev. B 73, 045428 (2006)

Publications in Conference Proceedings

1. “Photoluminescence from silicon nanocrystals formed by anodization of bulk crystalline silicon in the transition regime”, S. Gardelis, A.G. Nassiopoulou, Proceedings of the 5th International Conference on Porous Semiconductors-Science and Technology (PSST), Sitges-Barcelona, 12-17 March, 2006

Conference Presentations

1. “Fabrication of ordered SiO_2 dots on Si substrate through a porous alumina thin film”, V. V. Gianneta, M. Kokonou and A. G. Nassiopoulou, XVIII Greek Conference on Solid State Physics and Materials Science, Patra, September 2006
2. “High density of silicon nanocrystals nucleated on oxidized or non-oxidized stepped silicon substrates patterned by electrochemistry”, M. Kokonou, A. G. Nassiopoulou and K. P. Giannakopoulou, European Materials Research Society Spring Meeting (E-MRS), Nice, France, May 29 – June 2, 2006
3. “Doubly stacked silicon nanocrystal memory structures with improved charge retention time”, A. G. Nassiopoulou and A. Salonidou, European Materials Research Society Spring Meeting (E-MRS), Nice, France, May 29 – June 2, 2006
4. “Photoluminescence properties and passivation of thin porous silicon films grown in the transition regime”, S. Gardelis and A. G. Nassiopoulou, European Materials Research Society Spring Meeting (E-MRS), Nice, France, May 29 – June 2, 2006
5. “Quantum confinement and interface structure of large Si nanocrystals embedded in a-SiO_2”, E. Lioudakis, G. C. Hadjisavvas, P. C. Kelires, A. G. Nassiopoulou and A. Othonos, European Materials Research Society Spring Meeting (E-MRS), Nice, France, May 29 – June 2, 2006

Invited Talks

1. “Semiconductor quantum dots for nanoelectronic devices and on-chip integration”, A. G. Nassiopoulou (Invited Talk), third Workshop on functional materials, FMA 2006, September 17-23 2006, Athens, Greece
2. “Micro-Nanoelectronics-Nanotechnology. The world of the infinitely small”, A. G. Nassiopoulou (Invited Talk), 4th International Student Conference of the Balkan Physical Union, ISCBPU-4, Bodrum, 29/8-1/8/2006
3. “Lateral ordering of semiconductor nanocrystals within SiO2 for non-volatile memories and other nanoelectronic devices”, A.G. Nassiopoulou (Invited Talk), NANOMAT-2006, Antalya, 21-23.6.2006
4. “Silicon nanocrystal non-volatile memory devices”, A. G. Nassiopoulou (Invited Talk), SINANO Workshop, Montreux, 22/9/2006
5. “Lateral ordering of semiconductor nanocrystals within SiO2 for nanoelectronic devices”, A. G. Nassiopoulou (Invited Talk), 3rd Workshop N&N, Thesssaloniki, 10-12 July 2006
6. “Light emission from silicon: Reality or dream?”, A. G. Nassiopoulou (Invited Talk), 1st International Workshop on Transparent Conductive Oxides (IS-TCO 2006), Crete, 23-25 October, 2006

7. “Lateral ordering of semiconductor nanocrystals for memory applications”, A. G. Nassiopoulou (Invited Talk), Workshop on Silicon Nanodevices Beyond CMOS: Emerging Nanodevices, RWTH Aachen, Germany, 7 – 8 November 2006
8. “Microelectronics-Nanotechnology: Present status and future trends”, A. G. Nassiopoulou (Invited Lecture), University of Thessaloniki, 18/10/2006
9. "Quantum wires and dots, applications in Nanoelectronics and sensors", A. G. Nassiopoulou (Invited Lecture), University of Thessaloniki, 18/10/2006

Organisation of Conference

1. E-MRS IUMRS ICEM 2006 Spring Meeting – Organization of Symposium C: Silicon nanocrystals for nanoelectronics and sensors, Nice 29/5 – 2/6/2006, Chairpersons: A. G. Nassiopoulou, Ph. Fauchet, L. Lechuga, Edition of Proceedings to appear in Physica E

PhD theses

1. “Nanocrystalline silicon for application in non-volatile memories”, Doctoral thesis of A. Salonidou, Univerity of Athens 17/4/2006
2. “Arrays of semiconductor nanocrystals ordered in 2-D layers within SiO_2 for application in memory devices”, PhD thesis of A. Olzierski, Univerity of Athens 6/10/2006