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PEOPLE
MARIE CURIE ACTIONS

International Incoming Fellowships (IIF)

Call: FP7-PEOPLE-2011-IIF

PART B

“**NoVoSiP**”

B1 **Scientific and technological quality** . . . .
B1.1 Research/technological quality, including any interdisciplinary and multi-disciplinary aspects of the proposal . . . .
B1.2 Appropriateness of research methodology and approach . . . .
B1.3 Originality and innovative nature of the project, and relationship to the‘state of the art’ of research in the field. . . . .
B1.4 Timeliness and relevance of the project . . . .
B1.5 Host research expertise in the field . . . .
B1.6 Quality of the group/researchers in charge . . . .
B2 **Transfer of knowledge** . . . .
B2.1 Potential for transferring knowledge to European host and/or bringing knowledge to Europe. . . . .
B2.2 Transfer of knowledge objectives . . . .
B3 **Researcher** . . . .
B3.1 Curriculum Vitae for Peter I. Gaiduk. . . . .
B3.1.1. Research experience. . . . .
B3.1.2. Research results including patents, publications, teaching.
B3.1.3. Independent thinking, leadership qualities, and capability to transfer knowledge. . . . .
B3.1.4. Match between the fellow’s profile and project. . . . .
B3.2 List of relevant publications . . . .
B4 **Implementation** . . . .
B4.1 Quality of infrastructure/facilities and international collaborations of host
B4.2 Practical arrangements for the implementation and management of the project . . . .
B4.3 Feasibility and credibility of the project, including work plan . . . . .
B4.4 Practical and administrative arrangements and support for the hosting of the fellow . . . .
B5 **Impact** . . . .
B5.1 Potential for creating long term collaborations and mutually beneficial co-operation between Europe and the third country. . . . .
B5.2 Contribution to European excellence and European competitiveness
B5.3 Benefit of the mobility to the European Research Area . . . .
B5.4 Impact of the proposed outreach activities . . . .
B6 **Ethical Issues** . . . .

B1. S&T Quality

B1.1 Research/technological quality, including any interdisciplinary and multidisciplinary aspects of the proposal

Resume

The project *"**N**an**o**-**Vo**ids in Strained **Si**licon for **P**lasmonics"* ("NoVoSiP") aims at exploring the use of nano-voids and nano-dots prepared as plasmonic structures to enhance the efficiency of Si single-crystalline photovoltaic (PV) devices. Fabrication and experimental investigation of plasmonic structures in strained Si/SiGe multilayered structures will be carried out to enhance light harvesting in solar cells due to both near-field and far-field effects. The main idea behind the production of nano-voids and nano-dots is based on the ability of compressively strained thin SiGe alloy layers, incorporated in a Si matrix during epitaxial growth, to collect small-sized atoms (H, He, C) or vacancies, induced by irradiation. Further, thermal treatment results in the formation of nano-voids which are strictly assembled within the strained SiGe layers. The following key processes will be used: Molecular beam epitaxy of strained Si/SiGe/Si structures followed by irradiation with light ions (hydrogen, carbon) and rapid thermal treatment. This structure will then be additionally used as a template for segregation and self-assembling of metallic or carbon nano-dots. The fundamental investigations of the structural, optical and electronic properties of the strained Si/SiGe layers will be carried out with a range of available methods for structural, electronic and optical characterization. By placing the nano-voids and nano-dots in a highly doped emitter layer close enough to the p-n-junction that the near-fields will extend into depletion layer, the effects of the near-fields will be obtained. This will give a contribution to the electron-hole pair generation, and this will be additional to the far field effects. Being formed periodically, strained layers with self-assembled nano-voids or nano-dots will exhibit fundamentally unusual electronic and optical properties. These effects have not been previously experimentally studied in a solar cell configuration. The present system offers a unique configuration for such investigation.

Introduction

Efficient conversion of sunlight into electrical energy is of great technological importance for modern society and future generations. The synthesis of electronic materials which interact strongly with light has been a major activity within materials science for several years mainly driven by the society's need for high efficiency light emitters and absorbers such as light emitting diodes, laser diodes and photodiodes. Remarkable results have been achieved, in particular, with epitaxial growth of the so-called III-V materials, of which GaAs is a prominent representative, using ultra-high vacuum deposition techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). One of the main drivers for the synthesis of semiconducting materials with enhanced light interaction is the demand to build high-efficient solar cells. The influential report of the US Department of Energy "Basic Research Needs for Solar Energy Utilization" from 2005 [1] states:

To enable solar electricity from photovoltaics to be competetive with, or cheaper than, present fossil fuel electricity, costs likely require devices that operate above the existing performance limit of energy conversion efficiency of 32% calculated for single-junction cells. At present, the best single-junction solar cells have efficiencies of 20-25%. New concepts, structures, and methods of capturing the energy from sunlight without thermalization of carriers are required to break through this barrier and enable solar cells having efficiencies of greater than 50%.

The program laid forward in this report is very ambitious, and puts a strong pressure on materials science to develop highly light-absorbing materials. Solar cells having such high efficiencies are called 3^{rd} generation solar cells [2]. They do not yet exist (with the exception of tandem solar cells based on III-V semiconductors) but are under intensive research and development.

The maximal thermodynamic efficiency for the conversion of solar irradiation into electrical energy (called "the performance limit of energy conversion efficiency" in the above report) is limited by two major factors [3]: (1) The excess kinetic energy of hot carriers, produced by photons of energy higher than the semiconductor band gap, is lost as heat (via electron-phonon interaction), and (2) photons of energy less than the band gap are not absorbed. In the case of a standard solar cell based on crystalline silicon (so-called 1st generation Si-solar cell) the theoretical maximal efficiency is about 30%, and the first mentioned loss amounts to about 65% of the total loss and the last mentioned to about 25%. Two main methods for extracting the excess kinetic energy of the hot carriers are being discussed in the solar cell community [2]: (1) Generation of multiple electron-hole pairs per absorbed photon by impact ionization; impact ionization becomes an efficient process in nanocrystals because of the so-called phonon bottleneck in nanocrystals which is a result of the discrete nature of the electron-energy states, and (2) hot-carrier solar cells, which utilize selective electronic contacts to extract the hot carriers before they thermalize with the semiconductor lattice. Also for the capture of photons with energy less than the bandgap there are two main mechanisms being discussed: (1) The use of so-called intermediate-band materials [2] where the intermediate band is produced from, e.g., a high concentration of mid-gap levels or a high concentration of nanocrystals, and (2) excitation of localized surface plasmons after interaction of light with metallic nano-particles [4,5] or nanocavities [6,7], followed by energy transfer to a close-by semiconductor to generate e-h-pairs.

In the NoVoSiP project we plan to synthesize and study Si-based materials with embedded nano-voids which are either empty or filled with Sn or C, in which, potentially, multiple excitons can be generated, localized surface plasmons be excited, and which might create an intermediate band gap. The main emphasis, however, will be on the interaction between the near-field from localized surface plasmons and the surrounding silicon material.

There are many reasons for focusing on silicon for this project: Silicon is the second most abundant element in the Earth's crust accounting for about 26% of the matter by weight in the outer 10 miles of our planet; the silicon microelectronics technology is highly developed; silicon is not poisonous, and it has very good physical parameters including a band-gap size which matches the solar spectrum. For these reasons more than 90% of today’s photovoltaic production is based on silicon, and a significant - if not dominant - part of the future photovoltaic production is expected to be based on silicon. Another significant argument for choosing silicon for this project is the focus of both participating research groups: The Semiconductor Group at Aarhus University and Department of Physical Electronics and Nanotechnology at Belarusian State University have been studying the electrical and optical properties of silicon for more than 25 years. Hence, the groups and key researchers have the necessary expertise and equipment to attack problems related to silicon-based solar cells.

***Surface plasmons** are collective oscillations of the electrons in a conductor, leading to resonant interaction between incident light and the conductor. If the electron oscillations are spatially confined in, e.g., a small metallic nano-particle, we talk about localized surface plasmon resonances. A consequence of the excitation of localized surface plasmon resonances is significant enhancement of light scattering (far-field effects) as well as absorption, and a very strong enhancement of the local electromagnetic fields (near-field effects). The extension of this near-field depends on material parameters and wavelength of the exciting light, but is typically 10-20 nm.*

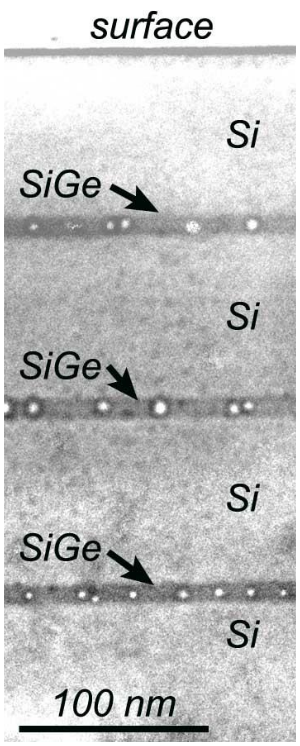
The project

A. Self-assembling of nano-voids

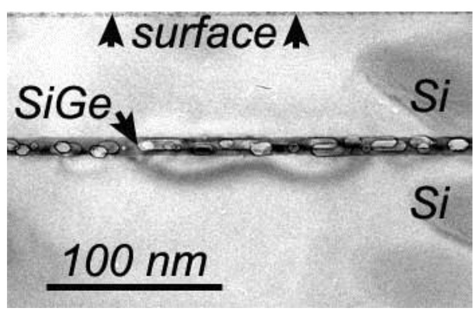
The approach taken in this project to produce nano-voids is based on the ability of compressively strained thin SiGe alloy layers, incorporated in a Si matrix during epitaxial growth, to collect molecules of small-sized dopants (H, He, C), vacancies (V) or vacancy-related defects (VRD), induced by particle irradiation. The accumulation of gas molecules, vacancies or vacancy-related defects in the compressively strained layer is then followed by a thermally activated formation of nano-sized voids which are strictly assembled within the strained SiGe layers (fig.1) [8,9]. This controlled formation of nano-voids within thin strained SiGe layers (quantum wells - QWs) buried in a Si matrix was first discovered by us some years ago using heavy particles irradiations [8-11], and has recently been studied by D'Angelo et al. [12,13] using He irradiations. Recently, our approach has been repeated for exfoliation process in smart-cut technology by using either hydrogen implantation [14] or hydrogen plasma treatment [15]. In this project we intend to further develop this approach for the formation of *self-assembled arrays of nano-voids* in Si/SiGe quantum wells.

It has recently been established that nanocavities in thin gold layers support localized surface plasmons, which couple strongly to incident light [7]. This effect manifested itself as sharp spectral features in reflection measurements. The resonance energies are easily tunable from ultraviolet to near infrared by controlling the size of nanocavities [7]. It was demonstrated in Ref. [6] that nearly total absorption of light occurs at the plasma resonance frequency of planar layers containing a two-dimension (2D) array of spherical nanocavities, and it was concluded [6] that absorption and local-field properties of these types of nanocavities can be effectively tuned by nanoengineering the spherical voids. In addition to this ***near-field effect***, voids-containing monocrystalline Si can trap light due to efficient light scattering (***far-field effect***). In particular, it has been recently experimentally demonstrated [16] that silicon solar cells with arrays of nano-sized holes have great potential for cost-efficient PV solar energy conversion.

Some years ago Li et al. [17] reported a remarkably high efficiency of 35% in a 1st generation Si-solar cell after high-fluence hydrogen irradiation and thermal annealing. Following an extensive public debate it was concluded that the result was probably based on misinterpretations of their measurements. However, the parameters used by Li et al. are known to create nano-voids in the highly doped emitter region [18], and, being confined in a highly doped (degenerated) semiconductor layer, these voids probably represent a suitable medium for localized surface plasmon formation and increase light scattering.



(a)



(b)

Fig.1. Under-focused bright-field cross-section TEM images of Si/SiGe structures, showing nano-void formation in SiGe strained layers as a result of:
(a) vacancy accumulation after implantation of 800 keV Ge^+ followed by thermal treatment at 990 C;
(b) accumulation of hydrogen after implantation and rapid thermal treatment.

Accumulation and storage of the vacancies and (or) gas atoms is due to a strong strain distribution around SiGe QW layers in a Si matrix. The epitaxial SiGe layer of under-critical thickness is compressively strained after growth. Thus, the assembly of the voids in a strained SiGe layer could be a strain-relieving phenomenon. This is supported by the void assembling within the SiGe QW layers as demonstrated in Refs. [8-11]. We believe that being formed periodically, such strained layers with self-assembled voids will display fundamentally unusual electronic and optical properties. This supposition was already tested in our previous study [8], which demonstrated a strong photoluminescence enhancement in the range of 1.4 – 1.55 μm, originating from the strained void-containing layer. Evidently this effect indicates the existence of new mechanisms of carrier – photon interactions near the voids. By placing the nano-voids in a **highly doped emitter layer**, but still close enough to the p-n-junction that the near-fields will extend into the depletion layer, the effects of these strong near-fields can be utilized and studied. The importance of the near field in the generation of electron-hole pairs has recently been addressed by Kirkengen et al. [19]. Their theoretical analysis indicated that the near field of nano-particles can excite electron-hole pairs without phonon assistance, the momentum being transferred to the nano-particle. This mechanism will give an extra contribution to the electron-hole pair generation compared to estimates that only take into account the far-field effects. To our knowledge, this effect has not previously been experimentally studied in a solar cell configuration. The present system offers a unique configuration for such an investigation.

B. **Self-assembling of metallic dots and carbon nano-particles**

It has been shown in many studies that voids are very efficient gettering sites for metallic contaminations and defects [20]. Due to their long stretched strain fields, voids attract and accumulate metallic contaminants and, under certain conditions, metallic nano-particles might be created by filling the empty volume of the voids. Thus, voids offer some new possibilities for formation of buried metallic nano-particles that can additionally absorb IR photons via the generation of localized surface plasmons.

A very nice example of this effect was given by Lei et al. [21], who demonstrated formation of Sn quantum dots during MBE growth of Sn_xSi_{1-x} ($0.05<x<0.1$) multilayers in a Si matrix. It was concluded by Lei et al. that diffusion of Sn atoms into the voids leads to rapid coarsening of α-Sn quantum dots during annealing. Thermal decomposition of MBE grown supersaturated SiSn alloy was investigated some years ago at the Semiconductor Group at Aarhus University and several interesting effects of formation of α-Sn and β-Sn precipitates were discovered [22]. The nanocrystals in the α-Sn phase are expected to have a direct band gap and a band-gap energy is strongly influenced by the size of the nanocrystal; α-Sn nanocrystals with band gaps between ~0 and 2 eV are theoretically possible [23]. Thus, this system is very promising for studies of multi-exciton generation in a Si - compatible system. Very recently we have extensively experimented with deposition and treatments of SiGe-Sn alloy layers and established optimal conditions for Sn nano-dot formation during oxidation-driven segregation (fig.2). This approach will also be used in our project-related studies.

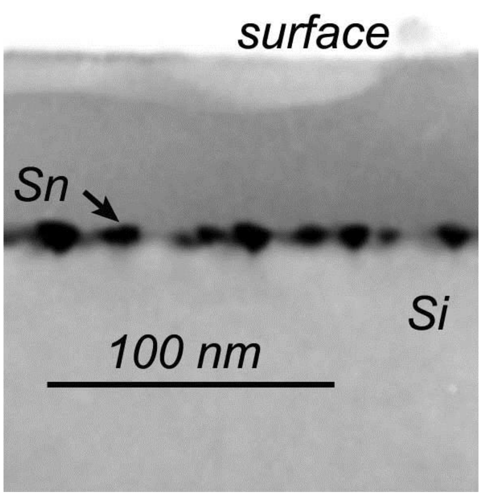


Fig.2. Bright-field XTEM image of self-organized small and homogeneous in size and shape Sn nano-dots after MBE growth of SiGeSn alloy layer followed by thermal oxidation at 925^{O}C for 60 min.

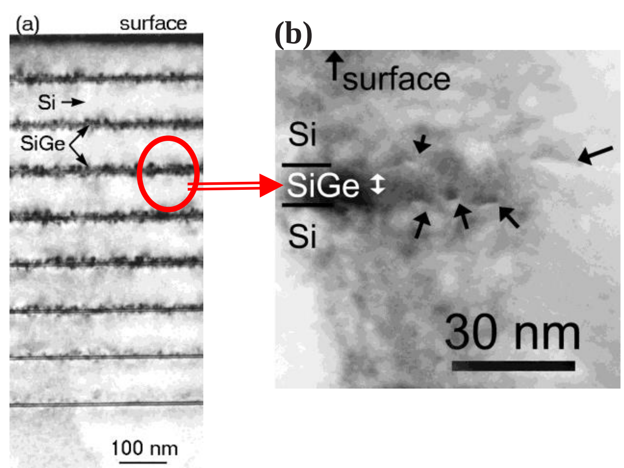


Fig.3. Bright-field XTEM images of Si/SiGe/Si multi-layered structure after treatment in carbon-containing plasma in “hot” conditions. (b) – magnified image of one of the layers. Arrows show platelets.

Carbon is another groupe IV element which is potentially interesting for photovoltaics: It has a number of different allotropic modifications, the most interesting being graphene. Recently, high quality graphene films have been synthesed by ion implantation of carbon in polycrystalline Ni [24]. The authors speculate that the graphene growth is driven by the surface properties and morphology of Ni grains. In our very recent investigation (to be published) we assumed that graphene plates may be formed around Si/SiGe/Si structures. The idea behind the study was that, due to a specific strain distribution, layers of Si/SiGe are attractive for segregation of foreign dopant atoms. If the dopant has a low solubility limit in Si, then there is a tendency for precipitation of the dopant atoms near the strained areas around structural defects. Phase and structural state of these precipitates depend on the configuration of the strain field. Usually, segregation of implanted carbon in bulk silicon results in tree-dimensional particles of graphite. However if the strain field is not isotropic, the shape of the precipitate might be different. We believe that a two-dimensional strain distribution in the case of Si/SiGe/Si heterostructure will dictate (**at certain strain distribution/conditions against surface orientation**) formation of plate-like precipitates of carbon and, probably, graphene plates. Fig. 3 represents XTEM images from our recent investigations, which displays the formation of such plate-like defects nearby Si/SiGe interfaces after “hot” implantation of Si/SiGe/Si multistructure in carbon-containing plasma. We found that plate-like defects contain carbon atoms; however more investigations should be done to clear up their structural state and phase type. We observed, however, that plasma treatment makes the surface darker, along with an improved photoconductivity, which let us to expect an increased absorption of light.

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