Research Article
A Combined Ion Implantation/Nanosecond Laser Irradiation Approach towards Si Nanostructures Doping

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The exploitation of Si nanostructures for electronic and optoelectronic devices depends on their electronic doping. We investigate a methodology for As doping of Si nanostructures taking advantages of ion beam implantation and nanosecond laser irradiation melting dynamics. We illustrate the behaviour of As when it is confined, by the implantation technique, in a SiO2/Si/SiO2 multilayer and its spatial redistribution after annealing processes. As accumulation at the Si/SiO2 interfaces was observed by Rutherford backscattering spectrometry in agreement with a model that assumes a traps distribution in the Si in the first 2-3 nm above the SiO2/Si interfaces. A concentration of 10^{14} traps/cm^2 has been evaluated. This result opens perspectives for As doping of Si nanoclusters embedded in SiO2 since a Si nanocluster of radius 1 nm embedded in SiO2 should trap 13 As atoms at the interface. In order to promote the As incorporation in the nanoclusters for an effective doping, an approach based on ion implantation and nanosecond laser irradiation was investigated. Si nanoclusters were produced in SiO2 layer. After As ion implantation and nanosecond laser irradiation, spectroscopic ellipsometry measurements show nanoclusters optical properties consistent with their effective doping.

1. Introduction

The future exploitation of semiconductor nanostructures (Si nanostructures in particular) depends on the understanding and control of their electronic doping. Doping of semiconductor nanostructures has proven to be distinct from the corresponding bulk materials [1–5] and recently great attention has been focused on developing practical methodologies to dope and control the doping properties of Si nanostructures such, as nanoclusters (NCs) [6–13] and nanowires [14–17], and on developing theoretical approaches to understand these properties [18–23]. The control of doping properties of Si nanostructures allows the fabrication of complex nanomaterials characterized by unprecedented electrical and optoelectronic functionalities.

In this work, we present a novel approach, based on ion implantation and nanosecond laser irradiations, to dope Si-based low-dimensional systems by As. In particular, two different types of Si low-dimensional systems are investigated relatively to their As-doping properties: a nanoscale Si layer embedded between two SiO2 layers and Si NCs embedded in SiO2. Concerning the former case, we illustrate the behaviour of As confined, by the implantation technique, in a SiO2(70 nm)/Si/SiO2(70 nm) multilayer and its spatial redistribution when conventional annealing processes are performed. Concerning the latter experiment, after the As implantation in the SiO2 layer containing Si NCs, laser irradiation was used to melt the Si NCs and to promote the As atomic incorporation in the Si NCs in order to achieve high doping level. Spectroscopic ellipsometry was
performed to investigate the effective As doping of the Si NCs.

2. Experimental

2.1. Samples Preparation

2.1.1. Nanoscale SiO$_2$/Si/SiO$_2$ Multilayer. The nanoscale multilayers were fabricated by sequential sputtering depositions of Si and SiO$_2$ using an AJA RF magnetron sputtering apparatus (Ar plasma, $5 \times 10^{-3}$ mbar pressure during the depositions). A multilayer SiO$_2$(70 nm)/Si(30 nm)/SiO$_2$ (70 nm) was grown on crystalline Si (c-Si), as shown in the scheme of Figure 1(a). During the depositions, the c-Si substrate was heated at 400°C. Then, two consecutive As implants, the first at 50 keV and the second one at 130 keV (at room temperature), were performed on such a sample. In this way, an As box profile centered in the Si layer, as suggested by TRIM simulations [24], was obtained. Three different total As fluences were realized: $2.5 \times 10^{15}$, $5 \times 10^{15}$, and $1 \times 10^{16}$ As/cm$^2$. After ion implantation, the samples were annealed by using a standard Carbolite horizontal furnace in dry N$_2$.

2.1.2. Si Nanoclusters in SiO$_2$. Si NCs were produced in a SiO$_2$ matrix following a standard procedure described in the literature [25, 26]; 200 nm thick substoichiometric SiO$_x$ (the Si excess is 6.3% atomic) was sputter-deposited (using the AJA RF magnetron sputtering apparatus) on c-Si substrate a. After a 1100°C-60-minute annealing (in dry N$_2$) a clustering process of the exceeding Si occurs. The net result is the formation of Si NCs of radius $r \sim 1.8$ nm, surface-to-surface distance of $d \sim 10$ nm and density $N \sim 9 \times 10^{17}$ cm$^{-3}$ embedded in SiO$_2$ (a scheme is presented in Figure 1(b)). 120 keV As implants with a fluence of $5 \times 10^{15}$ As/cm$^2$ were performed in order to obtain an As box profile in the SiO$_2$ layer. After ion implantation, the samples were processed by laser annealing. Laser irradiations were performed by a pulsed (10 ns) Nd:YAG laser operating at 532 nm (Quanta-ray PRO-Series pulsed Nd:YAG laser).

2.2. Characterizations. Rutherford backscattering analyses (RBS) were performed using a 2 MeV $^4$He$^+$ beam in normal incidence with a scattering angle of 165° and in glancing angle configuration (tilt angle of 64°) in order to improve the depth resolution. The RBS spectra were analyzed by the RUMP code [27].

Spectroscopic ellipsometry was performed in the 0.2–1 μm wavelength range in order to study the optical response of the samples. In particular, an effective medium approximation simulation analysis has been applied to the ellipsometric data in order to obtain both real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function [28–30].

Spreading resistance profiling (SRP) was performed in order to evaluate the dopant electrical activation after the annealing [31].

3. Results and Discussions

Figure 2 (a) reports the As concentration profile of the As-implanted ($5 \times 10^{15}$ As/cm$^2$) multilayer sample before (full line) and after (line with circles) annealing (950°C for 80 min). We can observe that before annealing, the maximum As concentration in the Si thin layer is about $5.6 \times 10^{20}$ atoms/cm$^3$. After annealing the As concentration in the Si layer decreases at a minimum of about $4.1 \times 10^{20}$ atoms/cm$^3$. The As diffuses through the Si layer towards the two Si/SiO$_2$ interfaces (indicated by the two dashed lines) where it is accumulated up to a maximum concentration of about $6.4 \times 10^{20}$ atoms/cm$^3$. Because of the very low diffusion coefficient of As in SiO$_2$ at 950°C, the As profile concentrations remain unchanged in the SiO$_2$ layers during annealing. The diffusion coefficient of As in Si at 950°C is much higher than in SiO$_2$: about $2 \times 10^{-14}$ cm$^2$/s in Si [32] (corresponding, after 80 min., to a diffusion length of 98 nm) and about $3 \times 10^{-18}$ cm$^2$/s in SiO$_2$ [33] (corresponding, after 80 min., to a diffusion length of 1.2 nm). The diffusion of As is hence inhibited in SiO$_2$ with respect to Si. Figure 2(b)
Figure 2: (a) As concentration profile in the nanoscale multilayer implanted with As fluence of $5 \times 10^{15}$ As/cm$^2$ before (full line) and after (line with circles) the 950°C 80 min annealing process; the dashed lines represent the Si/SiO$_2$ interfaces. (b) As concentration profiles for the nanoscale multilayers implanted with As fluence of $2.5 \times 10^{15}$, $5 \times 10^{15}$, and $1 \times 10^{16}$ As/cm$^2$ after the 950°C 80 min annealing process; the dashed lines represent the Si/SiO$_2$ interfaces. (c) “effective segregation coefficient” $C_{\text{max}}/C_{\text{min}}$, calculated as the ratio of maximum As concentration at the Si/SiO$_2$ interfaces and the minimum As concentration at the center of the Si layer, versus the As fluence. (d) Estimated values of the amount of As surface concentration trapped at each Si/SiO$_2$ interface as a function of the As-implanted fluence.

reports the As concentration profile of the three samples implanted with As fluences of $2.5 \times 10^{15}$, $5 \times 10^{15}$ and $1 \times 10^{16}$ As/cm$^2$ after annealing. The As depletion in the Si layer and the As accumulation at the Si/SiO$_2$ interfaces (represented by dashed line in Figures 2(a) and 2(b)) occurs for all the samples. We calculated an “effective segregation coefficient” $C_{\text{max}}/C_{\text{min}}$, for each sample, as the ratio between the maximum As concentration at the Si/SiO$_2$ interfaces and the minimum As concentration at the center of the Si layer. This coefficient is reported in Figure 2(c) as a function of the implanted fluence, and it quantifies the efficiency of the As accumulation at the Si/SiO$_2$ interfaces. The As accumulation process decreases its efficiency with increasing the implanted As fluence.

Several diffusion models have been proposed to describe the As redistribution in Si/SiO$_2$ systems during postimplantation annealing [34–38]. In these models, particular emphasis is devoted to consider the effects of the As-vacancy complexes on diffusion and/or electrical deactivation, but they do not predict the dopant accumulation near the surface [35, 37]. Ferri et al. [38] implanted As with energies between 1–10 keV both in samples with only the native oxide and in sample with a layer of 11 nm of grown oxide. Then, they annealed the specimens in N$_2$ atmosphere at temperatures
between 800 and 1025 °C for different times between 5 s and 4 h. They determined the As distribution in proximity of the samples surface by using secondary ion mass spectrometry and Z-contrast scanning transmission electron microscopy. In particular, an As pileup in the first nanometers of the Si matrix in proximity of the SiO₂/Si interface was observed. The phenomenon was explained with a “Fickian” standard diffusion by assuming the presence of “dopant traps” near the SiO₂/Si interface that cause a reduction of the dopant able to diffuse inside the bulk. Their results support the hypothesis that the As accumulation in proximity of the surface is due to a dopant trapping in energetically favourite places. Their simulations routine considers unpaired point defects and dopant-defect pairs as mobile species and the unpaired dopant on lattice sites as immobile species. A dopant atom cannot diffuse on its own; it needs the presence of a point defect (a silicon self-interstitial or a lattice vacancy in different charge states) in the near neighborhood as a diffusion vehicle. Introducing such a “traps” distribution into the Si in the first 2-3 nm above the SiO₂/Si interface, they obtained good agreements between simulation and measured profiles. Furthermore, their results demonstrate that the trapping behaviour of the region near the surface is not due to defects or impurities introduced by the implantation, but it is a property induced by the surface. On the basis of such a model, we could speculate that, in our samples, the accumulation of As at the two Si/SiO₂ interfaces is due to the formation of As-Si point defect pairs that diffuse through the Si towards the Si/SiO₂ interfaces where they are trapped (and accumulated) in energetically favourite places. Furthermore, the concentration of the traps at the Si/SiO₂ interface is an intrinsic characteristic of the interface and it has been estimated to be about 10^{14} traps/cm² by measuring the area of the As peaks in Figure 2(b) (grey areas), as summarized in Figure 2(d). This qualitatively explains the decrease of \( C_{\text{max}}/C_{\text{min}} \) for increasing the As fluence. In fact, the number of As atoms accumulated at the Si/SiO₂ interfaces is the same for all the samples independently on the As-implanted fluence; in the sample implanted with 2.5 \times 10^{15} As/cm², only the 4% of the total implanted As is accumulated at the interfaces, at this percentage decreases at 2% and 1% for the samples implanted with 5 \times 10^{15} As/cm² and 10^{16} As/cm², respectively.

Finally, on these nanoscale multilayers samples, SPR measurements were performed to evaluate the carrier concentration profiles. Figure 3 shows the measured carriers concentration in the multilayer sample implanted by 5 \times 10^{15} As/cm² after annealing (950 °C 80 min). The maximum carriers concentration in the Si layer is about 10^{18} cm⁻³, indicating ~1% of dopant activation after annealing.

The result concerning the surface concentration of As atoms (10^{14} cm⁻²) trapped at the interfaces of the SiO₂/Si/SiO₂ multilayer can be used to infer a crucial characteristic of the doping properties of Si NCs using ion beam techniques. Si NCs embedded in SiO₂ are widely investigated for their novel size-dependent electronic and optoelectronic properties [6–13]. In particular, the exploitation of the properties of such systems in real devices demands an accurate control of their doping. On the basis of the previous results, we can conclude that if we consider a Si NCs embedded in SiO₂ characterized by a radius of 1.8 nm, after As implant and annealing about 40 As atoms are trapped at the Si/SiO₂ interface. For a NCs density of 9 \times 10^{17} cm⁻³, an As concentration of 3.6 \times 10^{19} As/cm³ is trapped. This fact involves the implantation of As concentrations higher than 3.6 \times 10^{19} As/cm³ in order to have the chance that at least an As atom can be incorporated in a Si NCs for an effective doping. Alternatively to conventional annealing processes, we explored a laser annealing process in order to promote such a high As concentration doping of Si NCs. In particular, the idea was to use a nanosecond laser irradiation to melt the Si NCs so to promote the As atoms incorporation in the liquid Si NCs. In order to exploit this idea, the following experiment was performed: 200 nm thick substoichiometric SiOₓ (Si excess of 6.3 at%) was sputter-deposited on c-Si substrate. After a 1100 °C-60 minutes annealing (in dry N₂) a clustering process of the exceeding Si occurs. The net result is the formation of Si NCs of radius \( r \sim 1.8 \text{ nm}, \) surface-to-surface distance of \( d \sim 10 \text{ nm}, \) and density \( N \sim 9 \times 10^{17} \text{ cm}^{-3} \) embedded in SiO₂ [25, 26]. Then, a 120 keV As ion implant, at 5 \times 10^{15} As/cm², was performed to obtain As box profile in the SiO₂ layer. Finally, a single pulse laser irradiation process at 407 ml/cm², by a pulsed (10 ns) Nd:yttrium aluminum garnet YAG laser operating at 532 nm, was performed. Spectroscopic ellipsometry allowed us to evaluate the laser effect on the optical constants of the Si NCs without and with the presence of the As. Figure 4 reports the measured optical constants \( \varepsilon_1 \) (real part of the dielectric constant, related to the reflection coefficient) and \( \varepsilon_2 \) (imaginary part of the dielectric constant, related to the extinction coefficient). In particular, Figure 4(a) reports the optical constants measured for the system Si NCs/SiO₂, without As, after the 407 ml/cm² laser irradiation. \( \varepsilon_1 \) and \( \varepsilon_2 \) are showed as a function of the wavelength of the incident radiation in the 0.2–1 μm range, and the spectra of bulk Si are also reported for comparison (with the characteristic threshold at about 0.38 μm for \( \varepsilon_1 \) and at about 0.29 μm for \( \varepsilon_2 \)). The notable feature is a reduction of the optical constants of Si NCs with respect to the bulk.

![Figure 3: SRP carrier concentration in the nanoscale multilayer implanted with As fluence of 5 \times 10^{15} As/cm².](image-url)
Si. This reduction is characteristic of the Si NCs due to their reduced dimensionality, as already shown in the literature [29, 30]. In general, it has been well established that a reduction of the dielectric constants becomes significant as the size of the quantum confined physical systems, such as quantum dots and wires, approaches the nanometric range [29, 30, 39, 40]. However, the origin of the reduction in the dielectric constant with the size is still not fully understood. It is often attributed to the opening of the gap, which should lower the polarizability. Figure 4(b) reports the optical constants measured for the system Si NCs/SiO2 after As implantation and after the 407 ml/cm² laser irradiation. In this case, the notable feature is a shift of the peak of ε₁ for the NCs from 0.34 μm to 0.36 μm and a shift of the peak of ε₂ of the NCs from 0.32 μm to 0.34 μm. These wavelength shifts of ε₁ and ε₂ are clear signatures of the effective doping of the Si NCs and, to our knowledge, are the first observation of a similar effects in Si NCs. Instead, similar shifts were previously observed for the peak of ε₁ and ε₂ of bulk Si when heavily doped by n-type dopants such as P and As followed by pulsed-laser annealing [28]. This red-shift phenomenon in the optical constants of the Si NCs, in the presence of the As and after the laser irradiation process, is a signature of the effective doping of the NCs by As atoms since it is consistent with the introduction of localized states in the NCs bandgap. These localized states decrease the energy of absorbed or emitted photons, increasing, as a consequence, their wavelength.

4. Conclusion

As redistribution in a SiO2(70 nm)/Si(30 nm)/SiO2(70 nm) multilayer during postimplantation annealing produces an As accumulation at the Si/SiO2 interfaces. Such an effect is qualitatively in agreement with a model that assumes a “traps” distribution into the Si in the first 2-3 nm above the SiO2/Si interfaces. In particular, the traps concentration at the Si/SiO2 interfaces was estimated in 10¹⁵ traps/cm². This opens perspectives in the As doping of Si NCs embedded in SiO2. For example, a Si NC of radius 1.8 nm embedded in SiO2 should trap 40 As atoms at the interface. Therefore, to promote the As atoms incorporation in the NCs for an effective doping, a combined approach based on ion implantation and nanosecond laser irradiation was investigated. Si NCs, of radius of 1.8 μm and density of 9 x 10¹⁵ cm⁻³, were produced in a 200 nm thick SiO2 layer. After As ion implantation at fluence of 5 x 10¹⁵ As/cm² and 407 ml/cm² nanosecond laser irradiation, spectroscopic ellipsometry showed optical properties of the NCs consistent with their effective doping. These results indicate that such a doping approach deserves further investigations in order to develop a better control of the doping process of a wide-range class of Si-based nanostructures.

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References
