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Received: 2018-07-31
Accepted: 2019-03-22

Process: 1. First trial (Field and check) ✔
          2. Peer review       ☐
          3. Editing and three trials ☐
          4. Published online   ☐
STRUCTURE and CONTENT of $^{64}$Zn$^+$ ION HOT IMPLANTED and THERMAL OXIDATED Si

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Abstract

Impurity cluster formation in $^{64}$Zn$^+$ ion hot implanted and subsequently thermal oxidized Si substrates are studied. After implantation on sample surface and in sample near-surface layer the metallic Zn clusters with average size near 200nm on sample surface and clusters with size about 20nm in a sample body were created. After annealing at 700°C there was transformation from metal Zn clusters to its oxide form such as ZnO(core)/Zn$_2$SiO$_3$(shell) on a sample surface and conservation the metallic Zn phase in a sample body. We propose an explanation for this phenomenon by temperature dependence of the oxygen molecules diffusion in silicon body and zinc atom opposite moving to the sample surface during annealing.

Keywords: silicon, zinc, hot implantation, thermal oxidation, Zn and ZnO clusters

1. Introduction.

Nowadays the properties of metal and metal oxide nanoparticles (NPs) in semiconductor and transparent dielectric matrices are comprehensively investigated because their possible application in future opto/microelectronic devices [1]. Zinc oxide NPs play an important role since ZnO has wide direct-band gap of 3.37eV and large exciton binding energy of 60meV, so these NPs can be used in UV light-sources [2] and electro luminescence displays [3]. According to other ZnO properties one must note another possible application such as in solar cells [4], in gas and biosensors [5], in memory devices of new age (memristors) [6] and in spintronic due to ZnO NPs obtain the ferromagnetism even at room temperature [7]. Since up to now Si is widely used in microelectronics, Zn and ZnO NPs in Si substrate can play an important role, as recording unit may be formed in one chip with signal source, for example, gas sensor and processing unit of its signal in one Si chip, because their technology is compatible. Zn implanted Si was investigated earlier, in few groups [8-12]. Here we present the investigation of NP formation in $^{64}$Zn$^+$ ion hot implanted Si and subsequent annealing in oxygen atmosphere at elevated temperatures. The first short conclusion of this work was declared in [13].

2. Experimental.

The commercial single crystal CZ growth n-Si(100) substrates were implanted by $^{64}$Zn$^+$ ions with fluence of $5\times10^{16}$cm$^{-2}$ and energy of 50keV. Prior to implantation, standard chemical surface cleaning in organic solvents in an ultrasonic bath was carried out. A Zn ion beam was incident on the Si surface along the normal. During implantation the Si substrate temperature was constant and about 350°C. Test samples were isochronally subsequently annealed during 1h in O$_2$ atmosphere at temperatures ranging from 600 up to 1000°C with the step of 100°C. During annealing in oxygen atmosphere, the Si will
also be oxidized and the silicon oxide film grows on the surface of the silicon substrate. The optimal annealing temperature for ZnO phase formation, as shown by the studies performed was about 700°C.

Cross-section of test samples were visualized using scanning electron microscopy (SEM) MIRA3 (TESCAN) in secondary electron (SE) emission and back scattering electron (BSE) modes with energy dispersive spectroscopy (EDS) and equipment for element mapping.

Impurity and its compound in depth profiles were investigated by time of flight-secondary ion mass spectrometry (TOF SIMS) using SIMS-5 unit (Ion TOF GmbH). The crater etching with dimensions of 300×300µm² was made by Cs⁺ and O⁻ ion beams with energy of 1keV. The analysis was made by Bi⁺ ion beam with energy of 30keV and current of 1.2pA, raster dimensions were 100×100µm². Ion etching crater dimensions were measured using stylus profilometer Alpha Step D-120 (KLA-Tencor).

Visualization and idetification of precipitats with in depth control were carried out by scanning Auger spectrometer PHI-670xi (Physical Electronics). The electron gun with thermo-field emission (Shottky cathode) has the following parameters: the accelerating voltage 5kV, for spectra registrations the primary current was 10nA and for image obtaining in SE and Auger electrons it was 1nA, electron beam diameter was 50-100nm. Spectrometer has the ion gun with differential pumping (“lamp type”) for cleaning surface contaminates and for etching at profile Auger analysis. The ion gun parameters were: accelerating voltage 2kV, ion beam current 0.5µA, bend tilt 10° for polishing etching, ion beam diameter was less than 500µm.

The chemical state of elements was revealed by X-ray photoelectron spectroscopy (XPS) with excitation illumination by MgKα anode with energy of 1253.6eV using vacuum module based on Nanofab 25 platform (NT-MDT). The energy resolution of the SPECS Phoibos 225 spectrometer detector through the Ag 3d₅/₂ line for non-monochromatic X-ray MgKα irradiation was 0.78eV. For the XPS spectra in depth profile analysis was used. The surface was etching by Ar⁺ ion beam with energy of 3keV and diameter of 0.7mm. The Ar⁺ beam was stroked according the sample surface normal of an angle of 50°. The etching rate was about 1nm/min and the etching crater sizes were 2.8×4.0mm².

3. Results and discussion.

3.1. SEM-SE sample surface investigation with EDS analysis.

![Fig.1. SEM-SE image (a) and SEM-BSE image (b) of as implanted Si sample surface.](image-url)
On Fig.1a, b there are presented the SEM-SE images (topological contrast) surface and SEM–BSE (Z-contrast) image of as implanted sample. On this figure one can see the bright spots with average size 20-50nm. According to Z-contrast image we can say that these bright spots are Zn-contained clusters. The black contrast spots may certificate as surface pores. This our conclusions are confirmed by EDS spectroscopy, which showed that besides matrix silicon Si-K peak only the zinc implanted Zn-L and carbon contamination C-K peaks are presented. All errors of these element contributions are related to

![SEM-SE image (a) and corresponding EDS overlapping images of mapping: Si-Ka1 (b), Zn-La1_2, gray – C-Ka1_2 for as implanted sample.](image)

the technical characteristics of the used EDS equipment. Below, in Fig. 2a the SEM-BE (electron) image of the sample surface after zinc implantation and overlapping of EDS mapping for Si, Zn and C elements (b) are presented. This figure is another confirmation of our conclusions about the composition of clusters located on the silicon surface after implantation.

### 3.2. TOF-SIMS spectra and profiles study.

Fig. 3 show the spectra of zinc isotopes, oxygen and their compounds for as implanted state (a) and after annealing (b). On this Fig. there are presented the natural isotope composition (black) and experimental isotope composition (red). On Fig.3a one can see, that since during implantation we used the mass-separated technique, so the zinc isotope $^{64}\text{Zn}$ only was present in all samples. On Fig.3 one can see, that since during annealing we used oxygen atsmosphere the two oxygen isotopes were presented: isotope $^{16}\text{O}$ (generally) and isotope $^{18}\text{O}$ (less) in all samples. The presence of the oxygen isotope $^{17}\text{O}$ is negligible. The oxygen compounds, namely, SiO$_2$, SiO$^-$ and ZnO$^-$ are repeated the O$^-$ distribution form and really located near the substrate surface in depth down to value of near 10nm. All these compounds have their profile maxima on a sample surface.
Fig. 3. Spectra of Zn$^+$, O$^-$, ZnO$^-$ and ZnOH$^-$ isotopes; a) – as implanted, b) - after annealing.
On Fig. 3 one can see too, that generally speaking, in as implanted state we can detected the 9 isotope of ZnO\(^+\) (theoretical) and obtained 7 isotope of ZnO\(^+\) (measured). But really we obtained both ZnO\(^-\) with mass generally 80=64(Zn)+16(O)amu, and less 82=64(Zn)+18(O)amu (after annealing). In addition, we find in the mass-spectrum the ZnO\(^-\) isotope with mass 82, 85, 86, and 88amu. But we must note that this situation is not related to changes in Zn isotope or O isotope masses, but connected with presence of hydrogen in our samples and OH\(^-\) radical formation in sample. One can compare measured spectra for ZnO- and ZnOH\(^-\) and see, that they are almost equal each to another with a mass difference in 1amu, just on the mass of the hydrogen atom, and not on the mass Zn isotope atom (theoretical, black), as predicted by the program applied to the using TOF-SIMS device. This situation is not new and is known in the literature [14-16].

On Fig. 4 there are presented the TOF-SIMS profiles, which have a quality character besides Zn\(^+\),

which has a quantity value because of we exactly known a Zn implanted fluence (for as implanted sample). From TOF-SIMS investigations (Fig.4.a) follow that in as implanted state the Zn concentration distribution was spent along substrate depth down to 200nm with a maximum near the R\(_p\)=50nm (according to SRIM [17] calculation). The oxygen compounds ions, namely, SiO\(_2\), SiO\(^-\) and ZnO\(^-\) are repeated the O\(^-\) distribution form and really located near the substrate surface in depth down to value of near 10nm. All these compounds have their profile maxima on a sample surface.

After annealing at 700\(^\circ\)C one can see the few moving on Zn\(^+\) main concentration peak to a depth of 60nm and revealed another Zn\(^+\) concentration peak at a sample surface. Due to O\(_2\) molecules diffusion from atmosphere into deeper sample body the O\(^-\) profile shift to a deeper position (Fig 4). And all oxide ion profiles, namely, SiO\(_2\), SiO\(^-\) and ZnO\(^-\) move deeper from its position in as implanted sample too [18]. They already extend into the sample body to a depth of 50 nm. So, in finish reason due to TOF SIMS study follows that after thermal treatment in oxygen in near-surface layer down to depth of 50nm there are presented the mixture silicon oxide phase in the form of mixture SiO-SiO\(_2\) and

![Fig.4. Zn impurity and its compound in depth TOF SIMS profiles: as implanted (a) [13] and annealed at 700\(^\circ\)C (b).](image-url)
zinc element in the form of mixture Zn·ZnO phases. We must note that Zn$_2$SiO$_3$ ions were not yet detected by this method at all.

3.3. AES spectra and mapping.

On Fig.5 here are presented the Zn AES spectra for as implanted sample (a) and for sample annealed at 700°C (b). In as implanted sample (Fig.5) one can see that on the Zn AES spectrum minimum at energy position of 996eV increased with depth etching from surface to the depth of 60nm. And energy position of this minimum, namely, 996eV didn’t any shifted. From that follow that at a depth profiling the Zn atom was in neutral metallic state.

After annealing at temperature of 700°C the Zn AES spectrum value have 2 maximum: at a sample surface and in a sample body. On the other hand the energy position of Zn AES spectrum minimum varied from 990eV at a sample surface to 996eV at a depth of 60nm. That testified that on a sample surface Zn has a positive charge, and at depth of 60nm the Zn was in a neutral metallic state. I.e., on a sample surface the ZnO phase was presented, and the Zn oxidation degree continually decreased at moving in a sample body to the neutral state at a depth of 60nm.

On Fig.6 there are presented SEM-SE image of as implanted sample at a depth of 50nm. On this

![Image](image_url)

Fig.6. SEM-SE image (a) directly in the Auger spectrometer of as implanted sample at etching crater wall in two magnification (low (a)) and (high (b)) at a depth of 50nm.
image one can see the weak contrast between the bright spots on a gray background applied to a Si matrix. Despite the SE different contrast, the Zn concentration at points 1 and 2 slightly differ from each other: $4.2\text{at}\% \pm 0.05\%$ and $3.85\text{at}\% \pm 0.05\%$, respectively, according to errors of used measuring equipment. Therefore, at the Zn distribution mapping in Auger electrons the difference between points 1 and 2 is almost no detectable. A decrease of SE emission coefficient in gray spots can be caused by a difference in concentration of other elements, for example, oxygen or carbon, which we can’t detected due to their low concentration by using Auger electron spectroscopy.

SEM-SE image for the analysis of ion etching crater slope at a depth of 50nm (a) and Zn distribution mapping in Auger electrons (b) are presented on a Fig.7. In this case, we managed to get a slight contrast in the Zn concentration distribution and can obtain the Zn mapping. From this SEM-SE and Zn mapping in Auger electrons images followed presenting Zn contained NPs with spatial diameters of the order of submicron. It may be metallic Zn, ZnO or Zn$_2$SiO$_4$ phases NPs.

3.4. XPS spectra with depth analysis.
On Fig.8 there are presented the profiling Zn 2p$_{3/2}$ XPS spectra. From as implanted sample XPS Zn

![Fig.7](image_url)

**Fig.7.** SEM-SE image (a) and Auger electron Zn mapping (b) for just the same area for a sample annealed at 700°C.

![Fig.8](image_url)

**Fig.8.** Zn 2p$_{3/2}$ XPS spectra in depth profiling; as implanted (a) and annealed at 700°C (b) [13].
XPS spectra (Fig.6a) it is clear that the Zn XPS signal from the surface is very few and badly detected with maximum of 1022.4eV. The last value is testified about Zn° metallic phase and some surface contaminates. With depth increasing the Zn 2p3/2 XPS signal initially increases to a depth of 5nm at energy of 1021.8eV. Than it begins to increase and reaches a maximum at a depth of 60nm. At last Zn 2p3/2 XPS signal peak decreases at a depth of 80nm at just the same energy of 1021.8eV, which correspond to combine the neutral Zn° that testified about existence of the metallic Zn phases [19, 20], i.e. metallic Zn NPs were created in as implanted sample.

Zn XPS spectra for sample annealed at 700°C presented on a Fig.8b. This temperature was chosen because at 800°C there was beginning the transition from the of metallic Zn phase to the willemite Zn$_2$SiO$_4$ phase. From the these spectra follows that at the surface the Zn XPS peak located at energy of 1024.5eV, which corresponds to mixture compound of Zn$^+$ chemical state with surface contaminations (mainly hydrocarbons). This peak is particularly broad. Such a broadening is generally indicative of the presence of various Zn specimens in the sample or a broad spectrum is sometimes related to differential charging effects and spectral artifacts. The binding energy peak value 1023.6–1022.0eV (curves 2-8) may testified about existence in subsurface layer the two Zn phases, namely, ZnO and Zn$_2$SiO$_4$, i.e. ZnO(core)-Zn$_2$SiO$_4$(shell) NP structure in annealed sample. With depth increasing the XPS signal initially decreases, and even at a depth of 5nm with energy shift to a binding energy of 1023.6eV, and then begins to increase and reaches a maximum at a depth of 60nm at binding energy of 1022.6eV, and then decreased at a depth of 80nm at binding energy of 1021.8eV [21-22]. During this process one can see the permanent shift of Zn XPS peak in region of smaller binding energy. In this case, the position of Zn XPS peak at a depth of 80nm is the value of 1021.8eV, this corresponds to a neutral Zn atom. By another words, in a sample bode there is observed the metallic Zn phase.

The evolution of ZnO NPs during annealing in oxygen may be explained by temperature dependence of the O$_2$ molecules diffusion length $L$ in Si and Zn atom moving. According calculation upon formula $L=2\sqrt{D t}$, where $D$ is diffusion constant and $t$ is an annealing time. Here $D=D_o \exp(-E/kT)$, where $D_o=0.025c m^2/s$ and $E=2.43eV$ [23], the value $L$ at annealing temperatures 600 and 800°C during 1h makes correspondently 20 and 380nm. As Zn concentration maximum is about 40nm, so during annealing at temperatures lower than 600°C there was no any oxidation of metal Zn NPs. As annealing temperature is 700°C and higher the value $L$ is such that moved to sample surface Zn atoms can meet with O$_2$ molecules, which diffused from environment atmosphere through sample surface to its body. As a result of this meeting is oxidation of Zn NPs and creation of NPs with ZnO·Zn$_2$SiO$_4$ mixed phase. The direct confirmation of our conclusion about NP structure is presented on Fig. 3b of paper [12].

Using Gibbs energy values [24] on can right about Zn NP creation

$$\text{Zn (gas, i.e. atom)} \rightarrow \text{Zn (bulk metal)}$$

$\Delta G$ (Gibbs energy) (300K) = - 95kJ/mol
ΔG (1200K) = + 7kJ/mol

Conclusion: the metal Zn NPs are formed at room temperature by Zn implantation and collapse at high temperatures.

For Zn oxidation on can right

\[ 2Zn + O_2 \rightarrow 2ZnO \]

ΔG (300K) = - 320kJ/mol
ΔG (1200K) = - 225kJ/mol

Conclusion: ZnO NPs are stable both at low and high temperatures (by themselves without chemical environment, e.g., Si matrix).

For ZnO oxidation in a Si environment there is a transition to another phase:

\[ 2ZnO + Si + O_2 \rightarrow Zn_2SiO_4 \]
ΔG(300K) = - 31kJ/mol
ΔG(1200K) = - 28kJ/mol

Since all of the upper mention Gibbs energy is negative, the process in the presence of O₂ molecules with Si environment is spontaneously formed the most stable Zn contained phase, i.e., Zn₂SiO₄ [25]. This phase prevails over the ZnO phase after the heat treatment in O₂ at temperatures higher than 700°C in a Si matrix.

**Conclusion**

1) Si substrates were implanted by Zn⁺ ion with energy of 50keV and fluence of 5×10¹⁶/cm². During implantation substrate temperature was nearly 350°C. Then were spent the subsequently isochronally annealing during 1h in O₂ at temperature range of 600-1000°C.

2) After implantation on surface and in Si near-surface layer the metallic Zn clusters with average size on surface 20-50nm and NPs with size near 20nm in body were created.

3) After annealing at 700°C there was transformation from metal Zn phase to its oxide form such as ZnO(core)·Zn₂SiO₄(shell) on a sample surface and conservation the metallic Zn phase in a sample body.

**References**

