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STUDY OF ELEMENTAL DEPTH DISTRIBUTION IN THE MATERIAL $TiO_2/SiO_2/Si$ BY RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)

T. V. PHUC[1,2,3,†], M. KULIK[3,4], A. P. KOBZEV[3] AND L. H. KHIEM[1]

[1] *Institute of Physics, Vietnam Academy of Science and Technology, Hanoi, Vietnam*
[2] *Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Hanoi, Vietnam*
[3] *Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia*
[4] *Institute of Physics, Maria Curie-Skłodowska University, Lublin, Poland*

[†] *E-mail:* tvphuc@iop.vast.ac.vn

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Abstract. *In this study we investigated depth distributions of elements in the multilayer structures of $TiO_2/SiO_2/Si$ before and after ion irradiation. The samples were implanted with Ne^+, Ar^+, Kr^+ and Xe^+ ions. For each implantation the multilayer structures were irradiated by the ions with energies of 100, 150, 200 and 250 keV. The elemental concentrations in the samples were analyzed by the Rutherford Backscattering Spectrometry (RBS) method. It was found that the transition layers existed between the TiO_2 and SiO_2layers. Formation of these layers derived from the ion beam mixing that was occurred at TiO_2/SiO_2interface after irradiation process. The depth profiles show that thickness of the transition layers increased with the growing energy and atomic mass of the implanted ions.*

Keywords: Rutherford Backscattering Spectrometry (RBS), Multilayer structures.

Classification numbers: 68.49.Sf; 61.72.Ww; 68.65.Ac. .

I. INTRODUCTION

Implantation is the most typical application of ion beams in materials modification, this technology is widely used for doping of semiconductors as well as for the synthesis of buried compound layers. It is not only the implanted atom modifies the material, but also the energy deposited into the solid may result in significant changes. Ion beam mixing is one well known example of such effect. This phenomenon is the interaction of ions with target atoms that takes place at the interface separating two different materials. During this process the target atoms can be displaced from their lattice sites and relocated to the new positions if they were bombarded by the ions with high enough energy. The atomic displacements caused by ion produce the collision cascade effects and lead to the formation of transitional areas which may significantly influence to material structure and their properties. Therefore, analyzing the effects induced by ion beam on the interface modification has become an important research area and attracted the attention of a lot of research on various materials by different methods [1–4].

Among various photocatalysis, $TiO_2$is one of the most studied materials due to its advantages such as large chemical stability, avirulence and strong photo-induced oxidation. TiO_2 as a photocatalyst has been widely applied in the environmental and energy fields, such as self-cleaning surfaces, air and water purification systems, sterilization, gas sensor, hydrogen evolution and dye-sensitized solar cell [5–10]. However, TiO_2 has large band gaps at 3.2 eV, 3.02 eV and 2.96 eV for the anatase, rutile and brookite phases, respectively [11]. So that photocatalytic effects are restricted only for the ultraviolet region of the light spectrum. In recent years, numerous studies have shown that TiO_2supported on SiO_2 exhibits an enhanced photocatalytic activity that makes TiO_2/SiO_2 particularly attractive for catalytic application [12-14]. In this work, the modification at interfaces of $TiO_2/SiO_2/Si$ structures after implantation as a function of energy and atomic mass of the implanted ions using RBS method will be presented.

II. EXPERIMENT

RBS is the nuclear analytical method widely applied for the near surface layer of solid characterization. This method allows to determine composition, concentration and depth distribution of the elements that exist in the studied samples based on the basic concept of the elastic collision such as kinematic factor, scattering cross-section and the energy loss of particles. The wide use of RBS is due to its high sensitivity (typically in ppm for heavy elements and few at.% for the light elements). Depth profiles of the elements in studied samples can be calculated on the RBS spectra, with a great depth resolution in nanometer range RBS is not only used for thin mono-layer analysis but also for investigation of the multi-layer structures and the interface between the materials [15].

In this study there were two groups of studied samples of similar structures of $TiO_2/SiO_2/Si$, the thickness of TiO_2 and SiO_2 layers of the samples in the second group was smaller than that in the first group. Each group included 4 subgroups of samples implanted with four different noble ions Ne^+, Ar^+, Kr^+ and Xe^+. There were four samples in each subgroup that were irradiated by the same species of ion with different energies of 100, 150, 200 and 250 keV. Ion implantation process was performed on the UNIMAS ion implanter being at the disposal of Maria Curie-Skłodowska University [16]. For each implantation, fluency of the incident ion beam was the

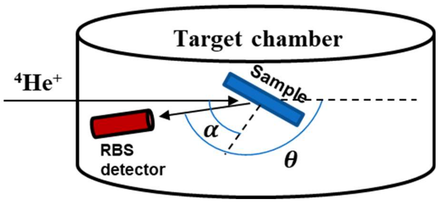

Fig. 1. The experimental set-up of RBS methods. α is the angle between direction of incident beam and the normal of sample surface, θ is the backscattering angle of ions after collisions.

same at 3×10^6 (ions/cm^2), the beams were perpendicular to surface normal of the samples. Depth distribution of elements in the samples before and after irradiation was investigated using the RBS method. The RBS experiments were carried out on the EG-5 accelerator at the Frank Laboratory of Neutron Physics, JINR [17]. He$^+$ ion beam with the energy of 1.5 MeV was used, the beam was directed to the samples under the incident angle $\alpha = 60^\circ$ towards the normal of the sample surface. The RBS spectra were collected at the scattering angle $\alpha = 170^\circ$ (Fig. 1) with energy resolution of spectrometric measurements was 15 keV. The elemental composition, their content and depth distribution were calculated using the SIMNRA code [18].

III. RESULTS AND DISCUSSION

Figure 2 shows the typical RBS spectra collected from the samples in the first group before and after implantation with Ne$^+$ ions at different energies of 100, 150, 200 and 250 keV. In these figures the vertical and slanted arrows indicate He$^+$ ions backscattered on the nucleons of the elements in the surface and in the sublayers respectively. There were the new peaks near the energy 550 keV associated with the presence of Ne$^+$ions in the samples after implantation. The significant reduction in the yields was found at the energy range related with O and Si for all spectra after irradiation. This effect corresponds to the presence of the doping ions result in decrease of O and Si concentration.

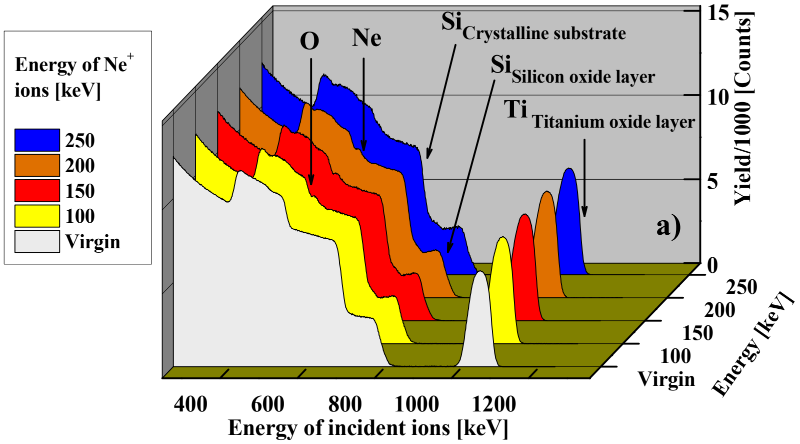

Fig. 2. The RBS spectra collected from the samples in the first group that were virgin and implanted with Ne$^+$ions at the different energies 100, 150, 200 and 250 keV.

It was observed that the left edges of the peaks related to Ti atoms which indicate for Ti at the interface of TiO_2/SiO_2 were shifted to both higher and lower energy range when the energy of incident ions were increased. In most cases, the edges shifted to the lower energy due to displacement of Ti atoms into the SiO_2 layers. Shifting of the edges to higher energy range can be explained by sputtering phenomenon. Besides that, shifting of the borders related with Si atoms to the higher energy was observed as well. This was associated with the displacement of Si atoms in the SiO_2 layers toward the TiO_2 layers through the interface. All of these effects

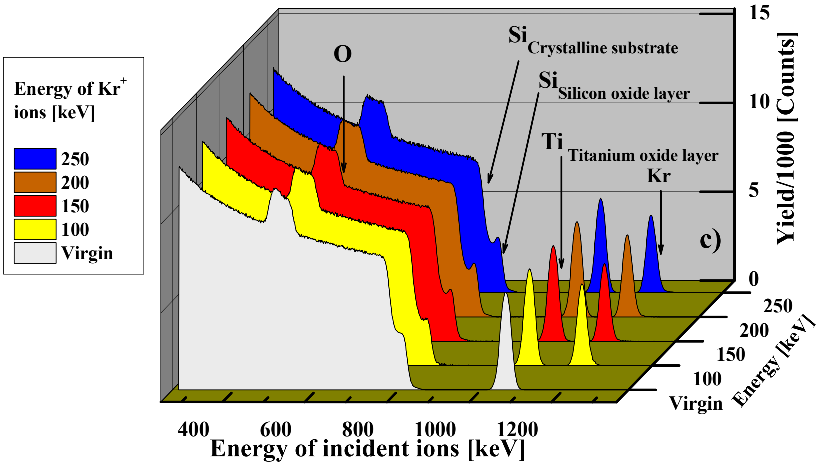

Fig. 3. The RBS spectra collected from the samples in the second group that were virgin and implanted with Kr$^+$ ions at the different energies 100, 150, 200 and 250 keV.

indicate to displacement of Ti and Si atoms at interface into the neighbor layers that made the real thickness of $TiO_2$and SiO_2 layers reduced. Moving of the displacements atoms leaded to forming of the transition area, when the ions energy was increased the thickness of TiO_2 and SiO_2 layers decrease results in broadening of the transition areas between these materials. The similar effects were also observed in the cases that the samples implanted with Ar$^+$, Kr$^+$ and Xe$^+$ ions.

The RBS spectra collected from samples in the second group that were virgin and implanted with Kr$^+$ ions are shown in Fig. 3. It was observed that these spectra possess the effects similar with cases the samples implanted by Ne$^+$, Ar$^+$, Xe$^+$ such as reducing of the bounds, appearance of new peaks and shifting of the borders after implantation. These effects were also observed in the spectra collected from the samples in the first group. However, there was significant difference in degree of changes between two groups of samples due to the difference in thickness of TiO_2 and SiO_2 layers.

By using SIMNRA code, the noticeable changes in the thickness of near-surface layers of the samples in both groups were determined. The relative changing thickness of the layers before and after ion irradiation were described by the equation (1). Since the atomic density of the layers was not known exactly, it was impossible to transform units of thickness from the atomic density into a nanometer scale. The thickness of the layers in the samples therefore was determined by the SIMNRA code with the unit of atoms/cm^2, as follows

$$r_t = \frac{t_{im} - t_{vir}}{t_{vir}}, \tag{1}$$

where t_r is the relative changing thickness of the layers,
t_{im} is the thickness of the layers after implantation,
t_{vir} is the thickness of the layers in the virgin samples before implantation.

The relative changing thickness r_t for the TiO_2, transition and SiO_2 layers of the samples in the first group that were implanted with Ne$^+$, Ar$^+$ Kr$^+$ and Xe$^+$ ions are shown in Figs. 4a, 4b, 4c and 4d, respectively. It was observed that the thickness of TiO_2 and SiO_2 layers decreased, accompanied by an increase thickness of transition layers when the energy of implanted ions was increased. This effect can be explained by growing of displacement atoms in the mixing area when the ion energies get higher. Appearance of disorders made the transition area expanded and led to the narrowing of TiO_2 and SiO_2 layers. The similar situations were observed in all cases when the samples were implanted with Ne^+, Ar^+ Kr^+ and Xe^+ ions. However, degree of changing thickness of transition layers increased respectively due to the fact that the atomic mass of implanted ions got heavier. In the case of the samples implanted with Ar^+ and Xe^+ions, although rising up of the fitting lines indicates to SiO_2 layers can be seen, it is evident that the whole of this lines located in the negative values of the vertical axis. This effect shows that the thickness of the SiO_2 layers decrease more than that of the virgin samples but with a declining degree when the ion energy grown.

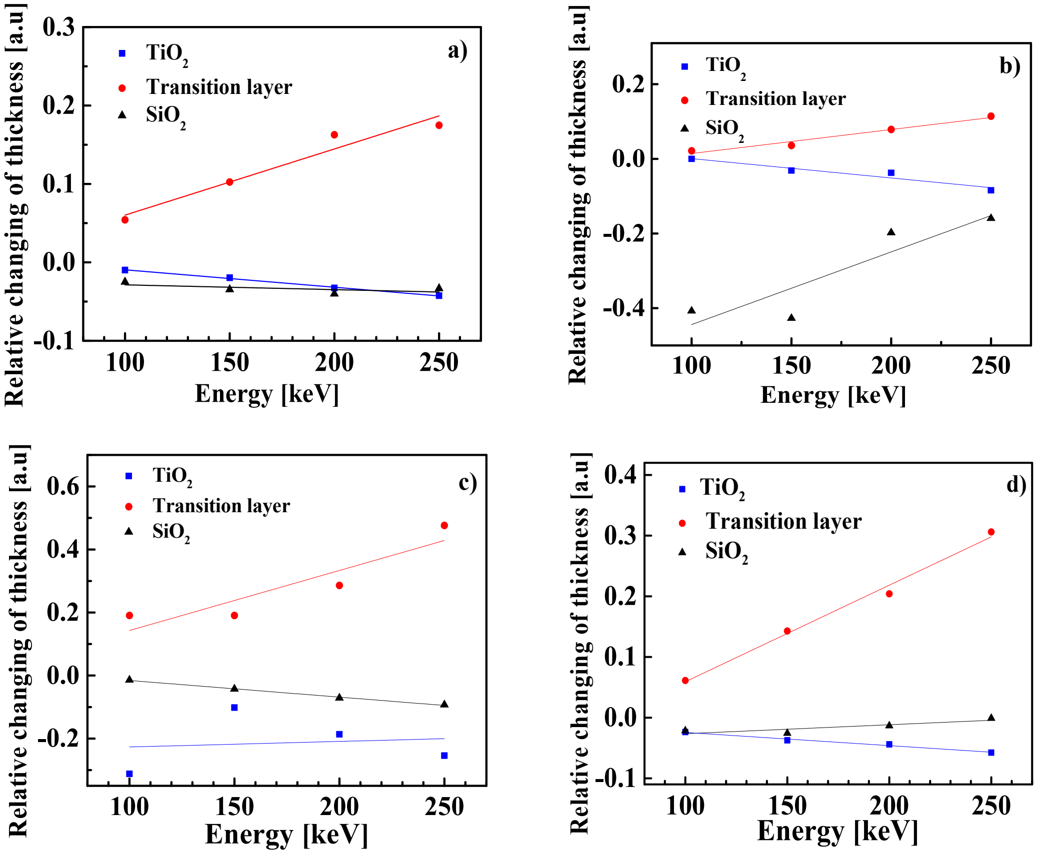

Fig. 4. Relatively changing thickness of TiO_2, transition and SiO_2 layers of two samples in the first group that were implanted with Ne^+ (a), Ar^+(b),_Kr^+ (c) and Xe^+ (d) ions.

In order to investigate changes of the layers with different thicknesses after ion irradiation, the samples in the second group were measured. For this group, thickness of TiO_2 and SiO_2 layers of the samples was lower than that of the samples in the first group. The relative changing thickness of the layers as a function of energy of the noble ions Ne^+ Ar^+, Kr^+ and Xe^+ is shown in Figs.5a, 5b, 5c and 5d, respectively. The variation thickness of the layers of the samples in the second group was similar with the first group. It was also observed that thickness of TiO_2 and SiO_2 decreased while that of transition layer increased with the growing implanted ion energy. However, in the case samples in both groups were implanted with the same type of ion, the thickness of transition layers of the samples in the second group was increased more than that of the first group. This effect can be explained by energy loss of the ions penetrating in thin TiO_2 films of samples in the second group less than the ions moving through the thick TiO_2 layers of the samples in the first group. Thus, the remaining higher energy created more disorders at the transition area between the TiO_2 and SiO_2 layers.

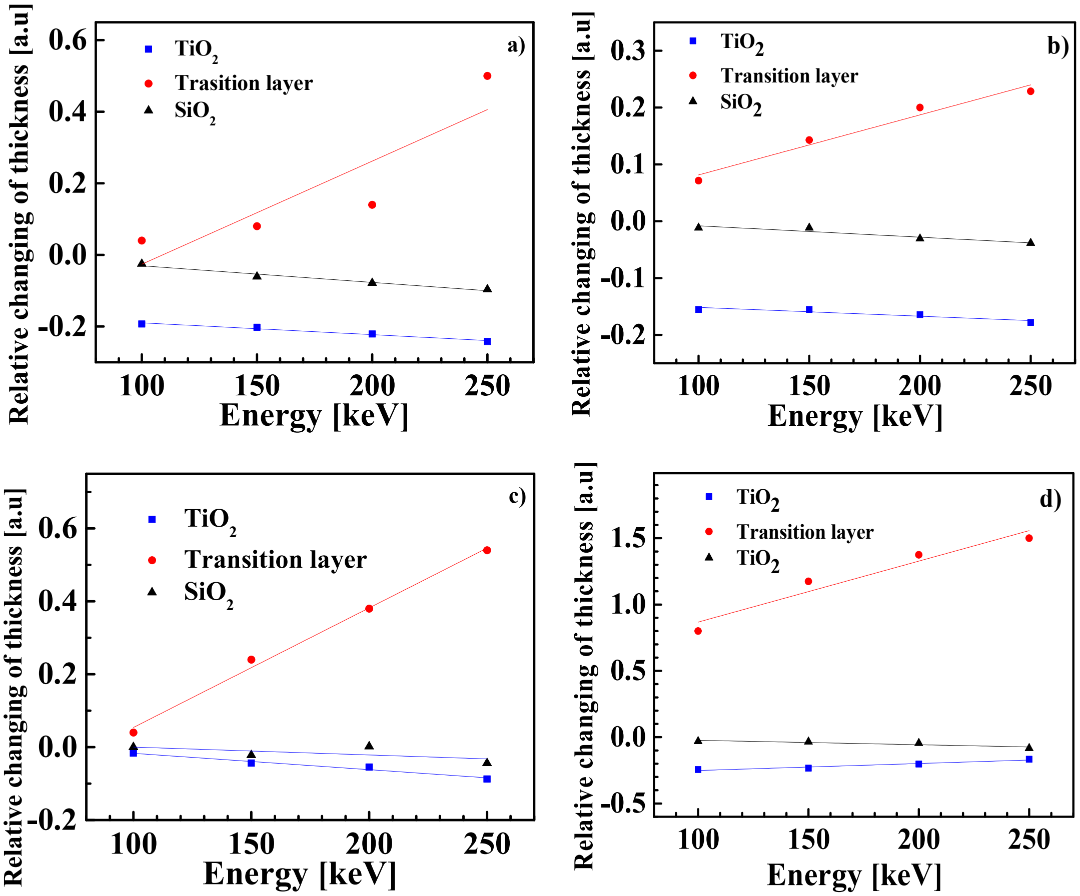

Fig. 5. Relatively changing thickness of TiO_2, transition and SiO_2 layers of two samples in the second group that were implanted with Ne^+ (a), Ar^+(b), Kr^+ (c) and Xe^+ (d) ions.

Figure 6 shows the relative changing thickness of TiO_2 (a) transition (b) and SiO_2 (c) layers of the samples in the first group as a function of the atomic mass of the irradiated ion at different energies. It can be seen that the thickness of the TiO_2 layer tends to decrease when the ion mass got heavier. However, the relation was not linear like the relative change of thickness as a function of energies. Thickness of TiO_2 layer decreased slightly in the case the samples were implanted with Ne^+, Ar^+ and Xe^+ions, the variation was greatest in the cases of Kr^+ implantation. The growing of atomic mass of ions made more disorders in samples and resulted in an increase in thickness of transition layers. The thickness of transition layers increased slightly in the case of Ne^+ and Ar^+ ions irradiation, reached the greatest changes with the Kr^+ ions and reduced degree when the samples was implanted with Xe^+. For SiO_2 layers the thickness was almost stable when the samples were irradiated with Ne^+ and Xe^+ ions, decreased slightly with Kr^+, and reached the largest drop in the case of Ar^+ implantation.

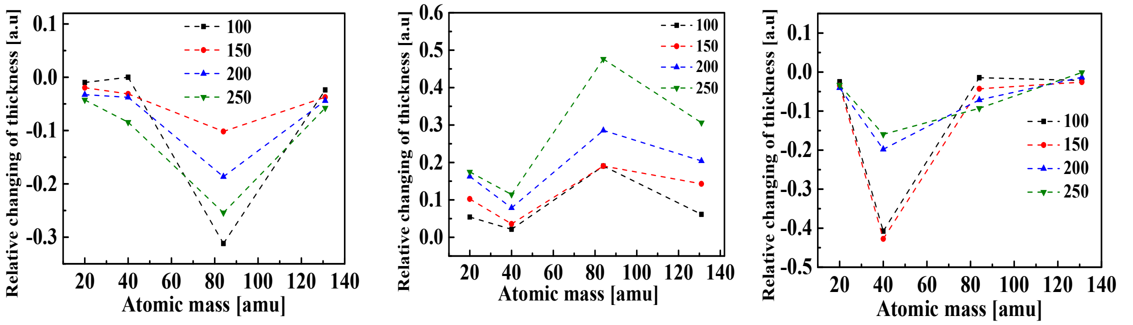

Fig. 6. The relative changing thickness of TiO_2 (a) transition (b) and SiO_2 (c) layers of the samples in the first group as a function of the atomic mass of the irradiated ions with different energies.

The relative change of the thickness of TiO_2, transition and SiO_2 layers as a function of the atomic mass of the irradiated ions with different energies for the samples in the second group can be seen in Fig. 7.

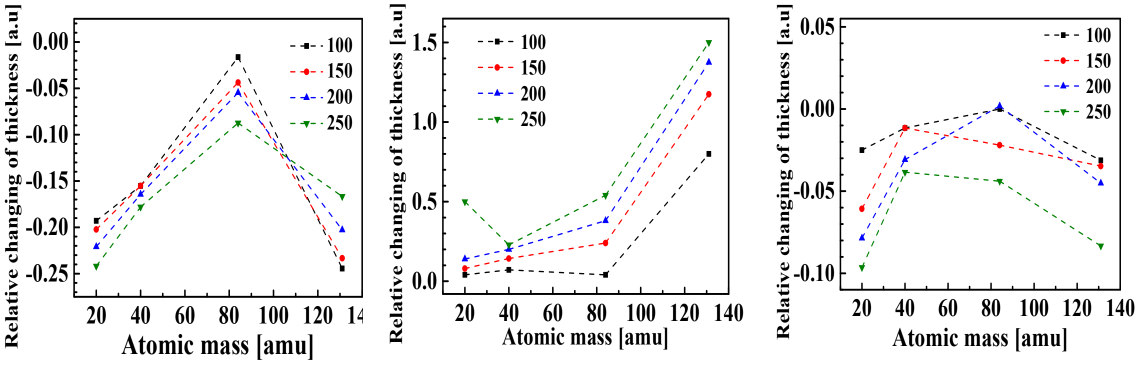

Fig. 7. The relative changing thickness of TiO_2 (a) transition (b) and SiO_2 (c) layer of the samples in the second group as a function of the atomic mass of the irradiated ions with different energies.

IV. CONCLUSIONS

In this study, the elemental depth distribution of the multilayer material $TiO_2/SiO_2/Si$ was investigated using RBS method. After irradiation of $TiO_2/SiO_2/Si$ samples with the noble ions at different energies, the concentration of the elements and structure of the near-surface layers were changed. The transition layers were formed at the interfaces due to ion beam mixing phenomenon. It was founded that thickness of the TiO_2 and SiO_2 layers decreased while that of transition layers increased with the growing energy and atomic mass of the implanted ions. The similar situation was observed for the structures with different thicknesses, however, it was noticed that the degree changing thickness of the thin layers was greater than that of thick layers after irradiation process.

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