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The role of high-energy electron irradiation induced defects in some mechanical properties of Si-SiO$_2$ structures

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The mechanical stress produced by 23 MeV energy electron radiation in both n- and p-type Si-SiO$_2$ structures is studied as a function of the dose. Low dose electron irradiation (2,4 – 4,8x10^{14} cm^{-2}) increases significantly the yield stress for n-type Si-SiO$_2$ samples, but to a much lesser extent for p-type ones. The nanohardness of irradiated structures is measured using the sclerometry method. Our results show that the nanohardness increases with the dose in the same manner for both groups studied. The values are very close, but for p-type samples are consistently higher. The variations of both the stress and nanohardness are remarkable at low doses. These mechanical properties of the irradiated samples are discussed on the basis of radiation induced defects.

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1. Introduction

Silicon-silicon dioxide structures are still widely used in microelectronics today, although novel configurations and compositions are constantly being introduced. The application of metal-oxide-semiconductor (MOS) structures in the contemporary semiconductor device industry is based on the fact that an extremely stable silicon/silicon dioxide (Si-SiO$_2$) interface with a low interface state density can be achieved. Electronic states at the Si-SiO$_2$ interface have been known to exert a profound influence on the properties of silicon interface-effects devices. The density of interface states, their capture cross section and time constants have been studied using different methods [1-5].

The study of the influence of different kinds of radiation on the electrical properties of Si-SiO$_2$ structures shows that the interface plays a key role in determining the electronic and optical properties of the Si-SiO$_2$ structure [1-8]. Radiation induced defects at the Si-SiO$_2$ interface, generated by high energy electron irradiation, also affect the mechanical properties of the structure. Specifically, an increase in the MeV electron irradiation dose is expected to show changes in any associated mechanical stress and nanohardness.

The present paper is a continuation of our previous work dealing with high energy electron irradiation induced defects on Si-SiO$_2$ interface [1-5]. This paper studies the influence of high-energy (23 MeV) electron irradiation induced defects in Si-SiO$_2$ structures on the yield film stress and nanohardness changes.

2. Experimental

n- and p-type Si substrates of <100> orientation were used. The silicon wafers of 330 μm thickness and of 4-6 Ω.cm and 12-16 Ω.cm resistivity respectively, were oxidized at 1050°C in a flow of dry oxygen, in order to produce a 10 nm thick oxide.

The Si-SiO$_2$ structures were subsequently irradiated by 23 MeV electrons. Irradiation was carried out in a Microtron MT-25, at the Flerov Laboratory of Nuclear Reactions of the Joint Institute of Nuclear Research (FLNR, JINR) Dubna, Russia. The beam current during irradiation was about 7-9 μA.

Table 1 presents all the electron doses, from 2.4x10^{14} to 2.48x10^{16} el.cm^{-2}, with which both groups are irradiated. Some of the samples were not irradiated, and were used as a reference.

In order to determine the mechanical stress changes in the films, produced by MeV electron irradiation, the radius of curvature of the Si-SiO$_2$ structures was measured before and after each irradiation dose, using the Newton's rings method with an adapted microscope [9]. The curvature change, (ΔK), was obtained, which in turn is proportional to the yield stress. With this technique, it was possible to determine not only the magnitude but also the bending direction of the Si-SiO$_2$ structures, and hence distinguish between the compressive and tensile stress. The error in the curvature determination was different for each sample, and thus for simplicity the highest error of 10% was taken as representative in all cases.

SiO$_2$ hardness measurements were performed by the method of sclerometry, before and after electron irradiation of the Si-SiO$_2$ structures. This method is in essence scratching the sample's surface at a constant load on the tip. The scratch width is the measured parameter that enters into the hardness calculation. For this purpose, a NanoScan (NS) system was used [10]. The scratch was done with a three-sided pyramid, "indenter edge forward", at 4500 μN load. The indenter for the sclerometry hardness measurements was simultaneously the tip employed for the surface scanning in a constant frequency mode. The tip calibration for the NS tests was set using an SiO_2 reference. The surface roughness was an order of magnitude less than the scratch dimensions. The typical error was about 15%, automatically assessed by the NS supplied software. It is noteworthy that the hardness measured by the sclerometry procedure with use of the NS was in good conformity with the Vickers hardness.

3. Results

Fig. 1 shows the curvature change of the $Si\text{-}SiO_2$ structures (ΔK), as a function of increasing 23 MeV electron irradiation dose. Fig. 2 presents the film nanohardness of the same $Si\text{-}SiO_2$ structures irradiated in the same range of doses. Each of the figures presents the corresponding characteristics of the n- and p- type $Si\text{-}SiO_2$ structures.

It is clearly seen in Fig. 1 that low dose electron irradiation (in the interval $2.4x10^{14}$-$2.4x10^{15}$el.cm^{-2}) strongly increases ΔK in n-type $Si\text{-}SiO_2$ structures. At the same time, the effect for p-type structures is minor. Doses of 4.8×10^{15} – 1.24×10^{16} el.cm^{-2}, start to reduce the value of ΔK for n-type material. At doses higher than about 5×10^{15} el.cm^{-2}, the changes seem to go more smoothly for both kinds of structure, but the values for n-type material decrease a little faster. The ΔK values corresponding to the mechanical stress are given in Table 1.

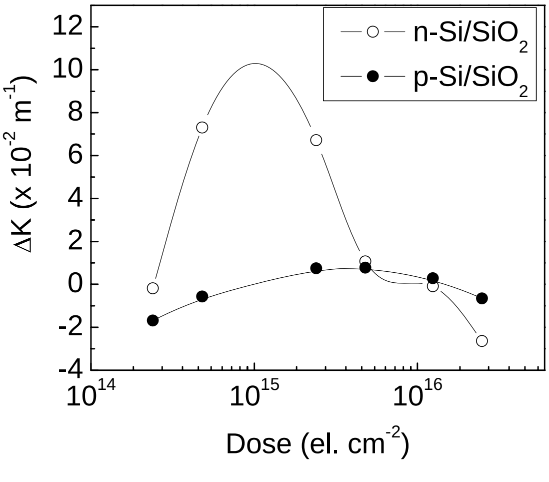

Fig. 1. Curvature change dependence of n- and p-type $Si\text{-}SiO_2$ structures irradiated with different doses of 23 MeV electrons. The curves are guides to the eye.

Table 1. Mechanical stress at different doses

Dose (el.cm^{-2})	Mechanical stress (GPa)	
	n-Si/SiO_2	p-Si/SiO_2
$2.40x10^{14}$	- 0.62	- 5.53
$4.80x10^{14}$	+ 23.90	- 1.85
$2.40x10^{15}$	+ 2.20	+ 2.47
$4.80x10^{15}$	+ 3.50	+ 2.57
$1.24x10^{16}$	- 0.31	+ 0.92
$2.48x10^{16}$	- 8.66	- 2.12

Fig. 2 presents SiO_2 the nanohardness dependence of both $Si\text{-}SiO_2$ irradiated structures. The points before the intercept of the curves for n- and p-type material depict the nanohardhess before irradiation. For all the doses and types, the nanohardness increases monotonically; the tendencies are similar, as the values are close. At the same time, the SiO_2 nanohardness of p-type samples stays higher than that of n-type.

It is worth mentioning that the nanohardness grows faster with respect to dose increase at low doses, in the same way as the stress change variations.

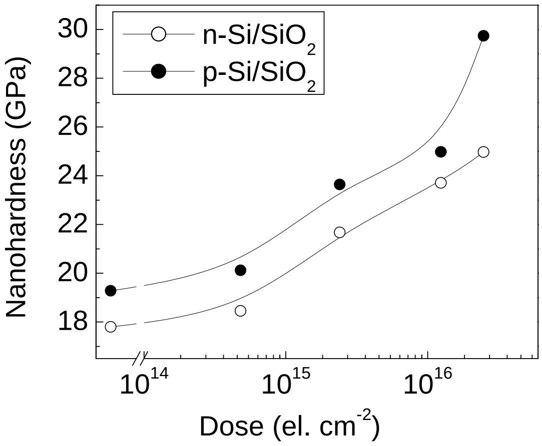

Fig. 2. SiO_2 Nanohardness dependence of n- and p- type $Si\text{-}SiO_2$ structures irradiated with different doses of 23 MeV electrons. The curves are guides to the eye.

4. Discussion

MeV electrons penetrate the $Si\text{-}SiO_2$ structures, and their energy is sufficient to produce hard radiation defects in the whole system. Such electrons are able to displace atoms from their normal positions in the semiconductor lattice of the substrate, resulting in the formation of a vacancy and an interstitial atom. When a vacancy diffuses through the lattice, it can be trapped by a variety of other defects to form a more stable defect – a vacancy pair.

These are a result of the interaction with donors, acceptors, interstitial oxygen and other vacancies, to form di-vacancies. When MeV electrons displace Si atoms with an energy of about several keV, they are able to knock out secondary low energy electrons. These low energy electrons could neutralize part of the positive charge in the oxide. The process of neutralization may also affect the oxide structure.

On the other hand, it is well known that the $Si\text{-}SiO_2$ interface is the most radiation-sensitive part of the structure. Our early studies show that the majority of the radiation defects induced by high-energy electrons at the $Si\text{-}SiO_2$ interfaces of the structures are associated with displacement of the main impurities in the Si substrate, such as phosphorus from n-Si (P/V) and boron from p-Si (B/V) [2,3]. So far, as these interface states generate structural changes at the $Si\text{-}SiO_2$ interface, we assume that stress changes would appear.

The present work has shown that the curvature change patterns for n- and p-type $Si\text{-}SiO_2$ structures after high energy electron irradiation are different, as can be seen in Fig. 1. This fact can be related to different kinds of radiation defect induced at the $Si\text{-}SiO_2$ interface in n- and p-type $Si\text{-}SiO_2$ structures, and the sequence of their creation.

The strong increase of the curvature change for n-type $Si\text{-}SiO_2$ structures at low dose electron irradiation (in the interval $2.4\text{x}10^{14}$- $2.4\text{x}10^{15}$ el.cm^{-2}) can be assigned to the generation of radiation defects like oxygen-vacancies (O/V) or di-vacancies. It has been reported that the concentration of these simpler defects initially increases and then decreases with increasing radiation dose [4]. Evidently, the curvature change follows the concentration trend of these simplest defects for the n-type structure. It has been further shown that with increasing irradiation dose, regrouping of the accumulating simpler defects into more complicated ones associated with the main impurities in the Si substrate occurs [4]. However, these results were demonstrated only for n-type $Si\text{-}SiO_2$ structures.

On the other hand, in the case of p-type $Si\text{-}SiO_2$ structures irradiated with high-energy electrons, it has been shown that radiation induced defects like boron-vacancy (B/V) complexes or interstitial Si atoms start to form, even at small doses [5]. The concentration of these radiation induced defects in p-type samples simply increases with increasing electron irradiation dose. We suggest that the almost equal concentration of basic impurities in both kinds of substrate (5-8 $\text{x}10^{14}$ cm^{-3}, [11]) will lead to almost equal ΔK values of both $Si\text{-}SiO_2$ structures at the highest electron irradiation dose. Thus, the mechanical stress in SiO_2 is dependent on the interface states of the $Si\text{-}SiO_2$ structures, introduced by high-energy electrons.

This is in agreement with the work [12] of Tandia et al. on the influence of the vacancy density in the substrate on the mechanical stress distribution in a $Si\text{-}SiO_2$ (α cristobalite) structure. They show that the interface defects generate a large stress in the region of the interface and a smaller stress in the oxide upper layers. They also find that the stress at the $Si\text{-}SiO_2$ region is maximal when the defect density is one defect per silicon unit lattice. At higher defect densities, the interface stress is smaller. The stress dependence on the defect density is weaker for the upper layers.

The results presented in Fig.2 show that the nanohardness of SiO_2 in n- and p- type $Si\text{-}SiO_2$ structures depends on the electron irradiation dose. This dependence can be also understood in terms of the radiation defects created by MeV electrons, not only at the $Si\text{-}SiO_2$ interface but also in the oxide. We suggest that secondary low energy electrons neutralize part of the positive charge in the oxide. In other words, the quantity of electrically active defects in the oxide decreases, which contributes to the SiO_2 network energy decrease. This could explain the oxide nanohardness increase.

On the other hand, in our earlier study, we have shown that the main defect (P/V) concentration in n-type structures is higher than that in p-type (B/V) for the same electron dose of irradiation [3]. This could be a reason for the observed lower oxide nanohardness for the n-type irradiated $Si\text{-}SiO_2$ structure.

5. Conclusions

The influence of high-energy electron irradiation induced defects on the mechanical stress and nanohardness of thermally grown SiO_2 on n-and p-type Si substrates has been studied. It is proposed that the curvature change (and hence the stress) patterns for n- and p-type $Si\text{-}SiO_2$ structures can be assigned to the main defects created at both $Si\text{-}SiO_2$ interfaces, P/V and B/V respectively. It is suggested that the nanohardness increase with electron irradiation dose is a result of a decreasing the positive charge in the oxide. The variation in the mechanical properties of both kinds of $Si\text{-}SiO_2$ structure, caused by MeV electron irradiation, depends on the main impurity in the silicon substrates.

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