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Ion implantation induced blistering of rutile single crystals

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ABSTRACT

The rutile single crystals were implanted by 200 keV He^+ ions with a series fluence and annealed at different temperatures to investigate the blistering behavior. The Rutherford backscattering spectrometry, optical microscope and X-ray diffraction were employed to characterize the implantation induced lattice damage and blistering. It was found that the blistering on rutile surface region can be realized by He^+ ion implantation with appropriate fluence and the following thermal annealing.

1. Introduction

Recently titanium dioxide (TiO_2) film has attracted much attention as one of the promising photonic materials due to its unique properties. Among the three different crystalline phases of TiO_2 at room temperature (rutile, anatase and brookite), rutile has the highest refractive index. Rutile single crystal is transparent over a broad wavelength range from the visible to mid-infrared [1]. In addition, rutile is a prospective nonlinear photonic material which has a high nonlinearity (its third order nonlinearity is 25 times higher than silicon) and low two-photon absorption for photons above 800 nm [2,3]. The high index and wide transparent window of rutile make it an attractive materials for high-refractive-index-contrast waveguides in case of photonic applications.

In the past many methods have been investigated to fabricate TiO_2 waveguide films on the substrate with low refractive index [4–8]. Low loss TiO_2 waveguides with amorphous or anatase structures have been fabricated by sputtering method on silicon dioxide [9]. Passive waveguides and ring resonator with sub-micron footprint have been demonstrated [7]. Molecular beam epitaxy method was used to form planar and ridge TiO_2 waveguides on sapphire [6]. He ions with energy of 2.8 MeV was implanted into rutile single crystal to form an optical barrier type optical waveguide. This waveguide is weakly guiding so that integrated optics structures with small footprint cannot be fabricated [8]. Other methods including sol–gel, pulse laser deposition have been investigated to fabricate TiO_2 films [10,11].

From the technical point of view, one of the most promising methods to fabricate single crystal TiO_2 film is the ion-cut (implantation induced splitting) technology which is suggested by Bruel [12–14]. A typical example is SOI waveguide. In this case, silicon is implanted with H ions under a certain fluence. The following annealing treatment can induce H_2 bubbles formation inside the material which will lead to blistering and crater on the surface. A uniform blistering in the whole surface (in another word, splitting) will form a silicon film with homogeneous thickness [15]. Similar process has been applied to other semiconductor materials including GaAs, GaP and so on. The He^+ ion implantation also can induce blistering. This is more practical in case of Oxide insulators. Lithium niobate on insulator (LNOI) has been realized by means of He^+ ion implantation induced splitting and wafer bonding [16]. The He^+ ion implantation induced blistering (splitting) has been proved to be a convincing way to fabricate high-quality crystal film.

The He^+ ion implantation induced blistering is the physical origin of splitting. Up to now there have been rare reports about ion beam induced blistering on TiO_2 (film and single crystal) [17]. Therefore it is demanded to prove that high efficient blistering can be achieved in rutile crystal after the He^+ ion implantation. In this letter, we report on the He^+ ion implantation induced blistering on rutile crystal. The implantation induced lattice damage around the projected range was also characterized to verify the blistering process.

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2. Materials and methods

Commercially available *z*-cut rutile samples, optically polished and cleaned, were implanted with 200 keV He^+ ions at the Institute of Semiconductors, Chinese Academy of Sciences. The implanted fluence were 1.3×10^{16} ion/cm^2 (S1), 2.3×10^{16} ion/cm^2 (S2), 3.5×10^{16} ion/cm^2 (S3), 5.3×10^{16} ion/cm^2 (S4) and 7×10^{16} ion/cm^2 (S5), respectively. The total implanted area in the target disk was 50×50 mm sq, which is defined by a metal aperture. The ion beam was electrically scanned on the sample in order to ensure a uniform implantation. In order to avoid channeling effects the samples were tilted 7° off the normal direction of the crystal surface. The implantations were performed at room temperature. After implantation each sample has been cut into two halves. The first group was characterized by the Rutherford backscattering spectrometry (RBS)/channeling. The second group has been annealed at different temperatures in air condition to observe the surface blistering. The annealing conditions were listed in Table 2. After each annealing process the sample was observed under the optical microscope to examine whether the blistering has occurred or not.

A Zeiss microscope (Axio Imager A2m) was used to observe the surface blistering of the samples after annealing. High resolution (HR) XRD spectrum were measured by D8-Discover (Bruker) with a single Cu Kα line of wavelength = 1.54056 Å and angular divergence of $\Delta\alpha$ = 12 arc second. X-rays generated from the germanium monochromator were diffracted from rutile atomic (004) atom plane.

3. Results and discussion

RBS/channeling is a well-known method to investigate the near surface quality of implanted crystal materials. For the present samples, the arrangement of atoms determines the properties of implanted rutile crystals. The detected ions scattered on the heavier atom, Ti, have higher energy, which means higher channel number. Therefore the yields from 170 to 340 channel were collected from the He^+ ions backscattered from the Ti atom of TiO_2 lattice. The RBS/channeling measurements were performed with a collimated 2.02 MeV He^+ beam. The samples were mounted on a high precision three-axis goniometer in a vacuum chamber. The goniometer can be tuned finely so that the orientation of the sample can be collimated to the He^+ beam. The backscattered He^+ particles were received by an Au–Si barrier detector with a detection angle of 165°.

Fig. 1 shows the RBS/channeling spectra of the as-implanted samples. The virgin and random spectra are also measured from the pure rutile wafer for comparison. Random spectra was obtained at a random (non-channeling) orientation (representative of a spectrum from an amorphous sample). The minimum yields of the surface region (around channel 320) are around 2% for virgin rutile, which means that our rutile samples have very good quality [18,19]. For the implanted samples, it is found that the yields of the surface region of implanted samples are nearly the same to the virgin one. There are also no surface peak can be found near the surface region. Therefore, we can conclude that the crystal quality of surface region of the implanted samples remains good after the implantation. The broad peaks in the spectra of the implanted samples between channel 175 and 250 show a lattice disordered region inside the crystal. This lattice-disordered region is induced by nuclear energy deposition process during the He^+ ion implantation. As can be seen from the figure, the lattice disorder in the damaged layer increases with the implantation fluence, but the increment is reduced. The height of S4 and S5 are nearly the same. It is reported that the dynamic annealing which is induced by the elevated temperature during the implantation can produce lower damage than the expected value [20]. We believed that the nearly same RBS/channeling yield of S3, 4 and 5 is resulted from dynamic annealing of He^+ ion implantation.

Fig. 2 shows the damage profiles extracted from the RBS/channeling spectrum of Fig. 1. Damage simulated by SRIM2013 was depicted in the figure for comparison. It can be found that the experimental depth of damage peak is in good agreement with the theoretical predication, which is located at around 680 nm beneath sample surface. The width of extracted damage profile from RBS is broader than that of simulated result. It may be caused by He^+ diffusion during the implantation and the low precision of the detector resolution.

Table 1
The summary of bubble formation and blistering of rutile samples with different fluence and annealing conditions.

Sa No.	An No.			
	1	2	3	4
1	I	I	I	I
2	I	I	I	I
3	I	I	I	I
4	I	I	I	I
5	I	BU	BU/BL	BU/BL

'Sa No.' for sample No., 'An No.' for annealing conditions summarized in Table 2, 'I' for intact, 'BU' for bubble formation under the surface, 'BL' for blistering in the surface region.

Table 2
The annealing conditions and the FWHM of the main peak of rutile samples.

No.	Annealing condition	FWHM	$\Delta\theta$
As implanted	As implanted	66.2″	554.4″
1	300 °C, 1 h	68.4″	554.4″
2	450 °C, 1 h	136.8″	367.2″
3	550 °C, 1 h	97.2″	NA
4	600 °C, 1 h	NA	NA

FWHM is the full width at half maximum of the main peak (004). $\Delta\theta$ is the deviation of the new peak compared to the main peak. NA means not available.

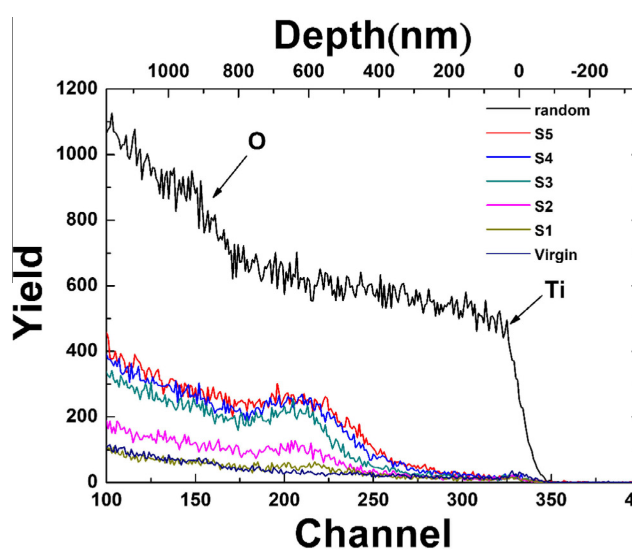

Fig. 1. The RBS/channeling spectra of He^+ ion implanted *z*-cut rutile with different fluence. The channeling spectrum of a virgin rutile crystal is also shown for comparison. The yield of channeling data around 210 channel increases with the implantation fluence, revealing that the lattice damage induced by He^+ implantation is accumulated under high fluence.