Ion implantation of MeV Au⁺ into potassium titanyl phosphate

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Received 24 January 2001, in final form 3 April 2001

Abstract

Potassium titanyl phosphate (KTiOPO₄ or KTP) was implanted with 1.0 MeV Au⁺ ions to a fluence of 5×10^{15} ions cm⁻² at room temperature under different angles of incidence. The longitudinal and lateral range profiles, diffusion, damage, surface morphology and structure have been studied by Rutherford backscattering (RBS)/channelling, scanning electron microscopy (SEM) and x-ray diffraction. The results show that (1) the experimental mean projected range is larger than the value predicted by TRIM (transport of ions in matter) by about 15%; (2) the experimental range straggling and lateral spread deviate from the TRIM predictions by around 50 and 20%, respectively; (3) the crystal is completely amorphized in the damaged region; (4) the implanted gold in KTiOPO₄ is stable against annealing at 700 °C, but diffusion takes place at and above 800 °C; (5) the surface morphology is different for virgin and Au⁺ implanted KTiOPO₄.

1. Introduction

Potassium titanyl phosphate (KTiOPO₄ or KTP) is an attractive optoelectronic material. Its high nonlinear optical d coefficients, high optical damage threshold, wide acceptance angles and thermally stable phase-matching properties make it a useful material in second harmonic generation (SHG) and waveguide fabrication of integrated optics [1]. Conventional methods such as diffusion and ion exchange have been used successfully to enable the generation of second harmonics and formation of optical waveguides in KTiOPO₄ [2–4].

Ion implantation has been used to alter the physical properties, such as the refractive index, of optoelectronic materials. It is a competitive technique for fabricating waveguides in a variety of electrooptic and nonlinear optical materials for integrated optical devices. The change in refractive index results either from the radiation damage or from the addition of impurity ions. The optical barrier in waveguides formed by ion implantation is related to the range and damage profiles. Ion implantation also induces changes in chemical composition, structural relaxation, and

phase conversion. We have used MeV He ions and heavy ions such as MeV F⁺ ions to form waveguides in KTiOPO₄ [5, 6]. The major change in refractive index in He⁺-implanted waveguides in crystalline materials is primarily due to collisional damage by the ion beam [7]. This damage causes a reduction in density of these crystalline materials, accompanied by a decrease in the refractive index at the end of the track [8]. After removing the radiation damage by annealing, these materials recrystallize. Therefore, studies on the range profile, damage and thermal stability of such ion-implanted optoelectronic crystalline materials are important. These data also test our current understanding of the range–energy relation, nuclear stopping cross section, nuclear scattering function, and the interatomic potential. Hitherto the investigations have been restricted mainly to the region of lower and medium energies in elemental targets, and only a few papers were published on MeV ions implanted in solids. To our knowledge, there are no reports on MeV Au⁺ implanted into KTiOPO₄.

In the present work we therefore attempt to investigate the range profile parameters of 1.0 MeV Au⁺ ions implanted into

Table 1. Overview of the first two moments of the distributions (in nm). Comparison of measurement with theory (SRIM 2000 and Biersack's original batch version T2D of 1991).

<i>T</i> (°C)	θ (°)	Version	TRIM deconvoluted		Measurement	
			R_p (nm)	ΔR_p (nm)	R_p (nm)	ΔR_p (nm)
RT	7	SRIM 2000	218.0	46.9	252.2	72.8
		T2D91	234.9	49.8		
	45	T2D91	162.5	42.5	166.0	62.5
	60	T2D91	114.0	38.9	114.0	56.7

KTiOPO₄ such as the mean projected range, range straggling and lateral spread. We also study the damage and diffusion behaviour of the implanted Au⁺ ions in KTiOPO₄ as well as the resulting surface morphology and structure.

2. Experimental

The KTiOPO₄ crystals with density 2.945 g cm⁻³ used in the present work were provided by the Institute of Crystal Materials, Shandong University. Samples with 1 mm thickness were cut along the (100) direction, polished and cleaned before implantation. The ion implantation was performed at the 1.7 MV accelerator of the Peking University. For this sake, the KTiOPO₄ samples were tilted 7° off the Au⁺ beam direction during implantation in order to avoid accidental channelling. Before implantation we used the Rutherford backscattering/channelling technique to measure the spectra at both random direction and 7° off the beam direction. The results show that both spectra are nearly the same. It is enough to avoid the accidental channelling at 7°. The present results are also consistent with those reported in [9] where the depth distributions of 1000 keV Xe⁺ implanted into KTiOPO₄ are nearly the same after amorphization and at 7° off beam direction. A beam current density of less than 50 nA cm⁻² at 1.0 MeV was used up to a fluence of 5×10^{15} ions cm⁻². In order to obtain the lateral spread of Au⁺ implanted into KTiOPO₄, tilted angle implantation was performed at 45 and 60° up to the same fluence. In all cases the samples were implanted at room temperature. Isothermal annealing of the samples in dry N₂ gas at 600, 700 and 800 °C for 30 min each was performed to study the diffusion behaviour of the implanted gold atoms in KTiOPO₄. During implantation, half of the sample was masked for comparative purposes.

The as-implanted and diffused Au depth profiles were measured by Rutherford backscattering (RBS) of 2.1 MeV He²⁺ ions at the 1.7 MV tandem accelerator of the Shandong University. The backscattered α particles were detected by a surface barrier detector placed at 165° to the incident beam direction. The Au surface position was calibrated by using a thin Au film deposited on a Si substrate. Further, the damage was studied by using the channelling technique. The surface morphology and structure of KTiOPO₄ were investigated by SEM and x-ray diffraction.

3. Results and discussion

Figure 1 shows the RBS spectrum of KTiOPO₄ implanted with 1.0 MeV Au⁺ to a fluence of 5×10^{15} ions cm⁻². The measured spectrum has four leading edges indicating Ti, K, P

Figure 1. RBS spectrum of KTiOPO₄ implanted with 1.0 MeV Au⁺ to a fluence of 5×10^{15} ions cm⁻². The four leading edges for Ti, K, P and O are marked.

and O. The energy-to-range conversion was performed using the 'RSTOP' subroutine of the TRIM program for ⁴He stopping cross sections [10].

As expected for heavy ion range profiles, the implanted Au⁺ profile has a shape close to a Gaussian. The mean projected ranges R_p and range stragglings ΔR_p are listed in table 1. The range straggling was obtained after deconvoluting the measured distribution, assuming that the system resolution and the He⁺ ion straggling were both Gaussian. This assumption makes sense, as the range profiles of heavy ions impinging into lighter solids are well known to have nearly symmetrical shapes with negligible skewness. Though there are no experimental data available on the energy straggling of He⁺ ions in KTiOPO₄, we can estimate it following [11].

The experimental values of R_p and ΔR_p are found to be 252.2 and 72.8 nm, respectively, and the corresponding values obtained by SRIM 2000 are 213.1 and 46.9 nm, respectively. Hence experimental values are larger than the corresponding theoretical values according to TRIM [12]; see table 1 and figure 2. The difference in R_p may essentially be attributed to errors in the knowledge of the stopping power of the gold ions in the given target, which vary from one TRIM version to the other. The actual ratio between the experimental and the predicted range straggling is approximately 1.5. The reason is not known. One possible reason is that this is not unexpected as effects such as charge state straggling are not taken care of in TRIM.

Please note that the measured Au concentration profile does not approach zero at greater depths, but shows a

Figure 2. Comparison of the experimental depth profile with the TRIM prediction for 1.0 MeV Au⁺ implanted into KTiOPO₄. The circles are the experimental data with the full curve representing the Gaussian fit. The histogram represents the TRIM prediction.

Figure 3. Depth distribution of 1.0 MeV Au⁺ implanted into KTiOPO₄ at target tilt angles of 45 and 60°, respectively. The open and full circles are experimental data for 45 and 60°, respectively. The full curves represent Gaussian fits.

low-concentration tail extending deep into the bulk. This tail is caused by event pile-up during the RBS measurement and to some extent also by multiple scattering of the backscattered He ions on their way out of the target. We used a low He beam current (around 2 nA) to remeasure the depth distribution of the implanted Au⁺ ions in KTiOPO₄ and the long tail almost disappeared. The depth distribution of 1.0 MeV Au⁺ ions implanted into KTiOPO₄ at 7° can be described well by Gaussian fit.

With the development of ion implantation devices with smaller dimensions, precise knowledge is needed not only of the depth distributions of the implanted ions, but also of their transversal distributions, which are governed essentially by the ions' lateral spread [13]. This information can be provided experimentally by tilted angle implantation, from which the lateral spread of the implanted ions can readily be deduced according to Furukawa and Matsumura's approach [14]:

$$(\Delta D)^2 = (\Delta R_p)^2 \cos^2 \theta + (\Delta X)^2 \sin^2 \theta \quad (1)$$

Figure 4. Comparison of depth distributions of 1.0 MeV Au⁺ in KTiOPO₄, as-implanted at room temperature (open circles), annealed at 700 °C (full circles) and annealed at 800 °C (open triangles).

Figure 5. Channelling spectra for 1.0 MeV Au⁺ implanted into KTiOPO₄ to a fluence of 5×10^{15} ions cm⁻². R represents the spectrum of random incidence. V and D are channelling spectra for virgin and damaged KTiOPO₄, respectively.

where ΔX is the ion's lateral spread which can be estimated from the measurements of ΔD at two different angles θ . This approach assumes that the spatial probability distribution of the deposited ions is a three-dimensional Gaussian, so that the depth distribution in a target tilted at an angle θ to the incident ion beam also becomes a Gaussian with the standard deviation ΔD . Figure 3 depicts the depth distributions of 1.0 MeV Au⁺ implanted into KTiOPO₄ at 45 and 60°, as obtained by RBS. As expected, the depth distributions of the implanted Au ions under different angles, 7, 45 and 60°, closely resemble Gaussians. The values of ΔD are again obtained from the measured standard deviation by taking into account the energy resolution of the measuring system and the energy straggling. The experimental lateral spreads are 42.8 and 41.2 nm, as obtained from either the 7 and 45° data set or the 7 and 60° data set, respectively. Both the theoretically predicted values for the lateral spread, ranging from 34.5 (SRIM 2000) to 37.0 nm (batch version T2D, 1991), underestimate the experimental lateral spread by around 20%.

Figure 6. SEM photographs of the surface morphology of KTiOPO₄, with magnification of 10000×. (a) Virgin KTiOPO₄; (b) KTiOPO₄ implanted with 1.0 MeV Au⁺ to a fluence of 5×10^{15} ions cm⁻² and annealed at 800 °C for 30 min.

Figure 7. X-ray diffraction pattern. (a) Virgin KTiOPO₄; (b) KTiOPO₄ implanted with 1.0 MeV Au⁺ to a fluence of 5×10^{15} ions cm⁻² after annealing at 700 °C for 30 min.

The data of table 1 have been fed into our modified tomographic reconstruction ('MOTOR') program to reconstruct the three-dimensional distribution of the implanted gold ions [15]. Figure 4 shows the thermal diffusion behaviour of 1.0 MeV Au⁺ ions implanted into KTiOPO₄ for different annealing temperatures. The peak positions of the depth distributions before and after the 700 °C annealing for 30 min are 252.2 and 252.3 nm, respectively. The standard deviations obtained before and after annealing are 72.8 and 71.4 nm, respectively. This comparison suggests that there is not yet any obvious mobility of the implanted Au ions in KTiOPO₄ at 700 °C.

After 800 °C annealing for 30 min, however, diffusion definitely occurs, as indicated by some slight broadening of the depth distribution. This change cannot be attributed, however, to regular Fickian diffusion, as we additionally observe a shift of the peak position from the range profile towards the nuclear damage profile, which rather suggests that the moving gold atoms are trapped at collisional defects. In fact, this model can be readily verified by performing a diffusion simulation [16], hereby assuming that the collisionally produced defects act as saturable traps. The best fit of such a simulation with the experimental findings indicates for the present case a diffusion coefficient of the Au atoms in the order of some $7 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ (with 70% accuracy) and a concentration of saturable traps in the order of $1.4 \times 10^{18} \text{ cm}^{-3}$ (with accuracy of about 70%).

RBS/channelling is a powerful technique to study the damage in solids created by ion implantation. The damage saturation can be caused from the amorphous layer or randomly oriented polycrystallinities. Figure 5 depicts the RBS/channelling spectra, in which R represents the spectrum for random incidence, and V and D are the channelled spectra for the virgin and damaged KTiOPO₄, respectively. The results show that the damaged region in KTiOPO₄ crystal is completely amorphized at the given fluence. This can be readily understood by a simple consideration: as nearly 104 vacancies are created per projectile ion according to TRIM (which does not take into account the vacancy recombination), one would arrive at a fluence of $5 \times 10^{15} \text{ ions cm}^{-2}$ at vacancy densities exceeding the atomic density of the target, which means damage saturation, hence amorphization. Hence the observation that the Au profile after 800 °C annealing can be simulated well by assuming a trap density of $\approx 10^{18} \text{ cm}^{-3}$ only means that considerable damage annealing has taken place already at this temperature.

Metallic ions implanted into optical materials at elevated fluence are supposed to cluster to colloids of nanometre size [17]. These clusters exhibit large third optical nonlinearities and fast time response. Shang *et al* reported on the optical characteristics of LiNbO₃ implanted with 23 keV Au⁺ ions [18]. They found the gold to precipitate after the implantation in the form of small clusters on the surface and metallic Au dots were observed on the surface. Scanning electron microscopy (SEM) was used to observe the surface morphology of our samples. Figure 6(a) shows the surface morphology of unirradiated KTiOPO₄, and figure 6(b) that of KTiOPO₄ implanted with 1.0 MeV Au⁺ ions and subsequently annealed at 800 °C for 30 min. The surface of the irradiated sample exhibits a structure with small grains which differs from that of virgin KTiOPO₄. But there is no Au aggregation to be

seen on the surface, suggesting that no colloids of Au are formed. This coincides with the absence of surface peak formation in the concentration profiles of figure 5. In the present case, the phenomenon is different from that of LiNbO₃. KTiOPO₄ has an orthorhombic structure with lattice constants of $a = 1.28148 \text{ nm}$, $b = 1.05888 \text{ nm}$, and $c = 0.64036 \text{ nm}$. Figure 7(a) shows the x-ray diffraction pattern from the virgin KTiOPO₄. The spectrum has three prominent lines corresponding to the KTiOPO₄ ($k, 0, 0$) directions with $k = 2, 6$ and 8 . Also we have observed the x-ray diffraction pattern of KTiOPO₄ implanted with 1.0 MeV Au⁺ ions to a fluence of $5 \times 10^{15} \text{ ions cm}^{-2}$. It was found that an additional two lines were observed which correspond to the (332) and (371) directions. Figure 7(b) shows the corresponding x-ray diffraction pattern of KTiOPO₄ implanted with 1.0 MeV Au⁺ up to a fluence of $5 \times 10^{15} \text{ ions cm}^{-2}$ after 700 °C annealing for 30 min. Nearly the same x-ray diffraction pattern as in figure 7(a) is observed.

4. Conclusions

We have used different methods to study the behaviour of 1.0 MeV Au⁺ implanted into KTiOPO₄ at a fluence of $5 \times 10^{15} \text{ cm}^{-2}$. These are RBS/channelling, SEM and x-ray diffraction. The main results obtained are as follows: (1) The depth distribution of the implanted Au⁺ ions is nearly of Gaussian shape. The experimental mean projected range is larger than the theoretical value by about 15%, and both the range straggling and lateral spread deviate from the TRIM prediction. (2) The RBS/channelling measurement shows that the KTiOPO₄ crystal is completely amorphized after irradiation at that given fluence. (3) The as-implanted Au⁺ in KTiOPO₄ is stable against annealing at 700 °C for 30 min. Diffusion takes place only when annealing at 800 °C for 30 min is carried out, and in this case the diffusion is governed by trapping at nuclear defects. (4) The surface morphology is different for the virgin and the Au⁺ implanted KTiOPO₄. No Au aggregation at the surface was observed after 800 °C annealing. (5) The x-ray diffraction patterns are nearly the same for the virgin KTiOPO₄ sample and the 1.0 MeV Au⁺ implanted sample after annealing.

Acknowledgments

This work was supported by the Hong Kong Research Grants Council Award HKUST 6127/97p and the National Natural Science Foundation of China (grant no 10035010). The authors would like to thank colleagues of the Ion Beam Research Laboratory at Shandong University, and Xue-Mei Wang from Peking University for their help.

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