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Direct combination of carbon structure with optoelectronics crystal: thermal behavior of implanted carbon in lithium niobate crystal at near surface

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Abstract

The thermal motion mechanism of carbon (C) in lithium niobate (LiNbO3) crystal was briefly studied, which provides experience and direction for the experimental parameters of graphene production by direct implantation of carbon ions into LiNbO3. Thin-film LiNbO3 crystal and bulk LiNbO3 crystal of z-cut were direct implanted by carbon ions with a dose of $1.14 \times 10^{16} \text{ cm}^{-2}$ and then annealed at different temperatures, thin-film LiNbO3 at 700 °C and bulk LiNbO3 at 900 °C. The experimental conditions and parameters of ion implantation and annealing were all the same except the annealing temperature. The samples were characterized by RBS, XRD, EDS and Raman spectrum. The results show that during annealing, the implanted carbon ions aggregate into clusters while moving towards the surface. This behavior prevents the carbon ions from precipitating on the LiNbO3 surface, which is not conducive to the production of graphene. The formation of graphene on LiNbO3 surface by direct ion implantation can only occur when implanted C dose and annealing temperature lie in a specific range.

1. Introduction

Graphene, a new type of two-dimensional material, was successfully prepared for the first time by the A K Geim team of the University of Manchester of UK [1]. Its special structure, outstanding properties have aroused great interest in the scientific community and become a research hotspot in material science [2–5]. As a monoatomic layer material, the carriers of graphene have extremely high mobility at room temperature [6, 7], which makes it have great potential in nanoelectronics, especially in high frequency applications. In the optical field, graphene also has unique properties, such as its strong restriction on the surface plasmon excitation in terahertz and infrared bands, and its high transmittance over the wide spectrum range from visible to infrared bands [8]. At the same time, graphene is one of the materials with the highest mechanical strength because its covalent bonding between carbon and carbon [9, 10]. With high light transmittance, wide tunable range and excellent mechanical strength, graphene is considered as an important material for future micro-nano electronic, photoelectric and photonic devices. The conductive properties of graphene can be adjusted by means of the photosensitive or thermostimulated properties of the substrate material in contact with graphene to achieve the functions of recording, storage or imaging, which has become an important part of the research on the application of two-dimensional graphene [11, 12].

As the “silicon material in the optical field”, LiNbO3 crystal film have the properties of piezoelectric, ferroelectric, polarized and so on. The combination of two-dimensional graphene and LiNbO3 crystal will have new and unexpected properties [13, 14], which is bound to have important research value.

There have been many reports on the synthesis of graphene in the last decade. The synthesis methods of graphene mainly include mechanical exfoliation method [1], epitaxy method [15], redox method [16], chemical vapor deposition method [17], and ion implantation method [18]. The ion implantation method has many
advantages, such as the number of layers of graphene can be controllably synthesized by precisely controlling the implantation dose and no requirement for carbon solubility of the material being implanted \[18, 19\], which makes it attracted much attention in recent years.

At present, the transition metal nickel (Ni) or copper (Cu) is usually used as catalyst for the formation of graphene by carbon implantation. Researchers usually implant the carbon that its dose is equivalent to the carbon content of one to four layers of graphene into nickel or copper film, after annealing, the carbon precipitates from nickel or copper film to form graphene \[18–25\]. However, in the method of forming graphene by ion implantation, removing the intermediate process of transition metal as a catalyst will be more attractive. It has become a new research idea to synthesize graphene by directly implanting carbon ions into crystals and then annealing to realize the precipitation of carbon on the surface of crystal.

The thermal diffusion of carbon ions in nickel and copper has been well studied \[26–30\], which constitutes the experimental basis for ion implantation to form graphene. However, direct carbon implantation of LiNbO₃ crystal and its thermal diffusion behavior have rarely been researched.

2. Experimental

Thin-film LiNbO₃ crystal and bulk LiNbO₃ crystal of z-cut were direct implanted by carbon ions and then annealed at different temperatures. The implantations were performed with the LiNbO₃ surface being tilt 7 degrees off the ion beam direction to prevent channeling effects. By referring to the parameters of C implantation of Ni to form graphene, the fluence of carbon ion implantation used in this paper is \(1.14 \times 10^{16} \text{ cm}^{-2}\), which is selected to match the carbon content of three-layer graphene. The implantation energy should be small enough to reduce the thermal motion distance of the C ions, however, the lower energy will lead to more serious sputtering on the surface of LiNbO₃. To balance these two aspects, the ion energy of 30 keV was chosen to keep total sputtering yield at a low level while ensures that the implanted carbons were distributed near the LiNbO₃ surface. Thermal motion mechanism of carbon ions in LiNbO₃ crystal was studied in two LiNbO₃ samples: one is the thin-film LiNbO₃ crystal with thickness of about 290 nm on 2 μm SiO₂ film and silicon substrate from top to bottom; the other is the bulk LiNbO₃ crystal with a thickness around 500 μm. Sample composition and the simulated carbon distribution is shown in figure 1. The distribution of carbon ions along the depth profiles was simulated by SRIM (Stopping and Range of Ion in Matter) and it comes out that the peak concentration of carbon is approximately at depth of 65 nm from surface. Implanted carbons in both materials are limited in LiNbO₃ crystal and present near Gaussian distribution.
Thermal behavior of carbon in LiNbO₃ is studied by post-implantation annealing. By referring to the diffusion of implanted C in Ni and Cu, which usually requires a temperature around 900 °C [18–25], the highest temperature in the present experiment is set at 900 °C. However, considering that the different LiNbO₃ samples have different tolerance to high temperature environment, thin-film LiNbO₃ crystal and bulk LiNbO₃ crystal were annealed under different temperatures. The maximum annealing temperature of thin-film LiNbO₃ was limited to 700 °C to prevent LiNbO₃ film from falling off the substrate in a higher temperature ambient and bulk LiNbO₃ was 900 °C. Except for temperature, the other annealing conditions are all the same. The samples were loaded into a quartz boat and heated in furnace to a certain temperature at a rate of 10 °C min⁻¹, then the temperatures were kept for 30 min and dropped to room temperature naturally in the same furnace. The whole process was performed under N₂ atmosphere, the pressure and flow rate were kept constant at 6 × 10⁴ Pa and 100 sccm, respectively.

3. Experimental results and discussion

The thin-film LiNbO₃ and bulk LiNbO₃ before and after carbon ion implantation were characterized by Rutherford backscattering (RBS) with a 2.1 MeV He ion and a detector positioned at about 165 degrees off ion beam to detect the backscattered ions. Figure 2(a) shows the channel spectra of thin-film and bulk LiNbO₃ before ion implantation. As can be seen in the figure, there are small spikes at surface on both the thin-film and the bulk LiNbO₃, which is caused by surface defects of the two materials. For the thin-film sample, defects-related spike also can be found at the interface between the LiNbO₃ film and the SiO₂ film substrate. And the edges correspond to the elements Si and O of substrate are indicated at the channel number of 200 and 100, respectively. The channel spectra of as-implanted samples are shown in figure 2(b). A new peak, corresponding to the ion implantation depth of 65 nm in SRIM simulation, emerged at the channel number of 397 for bulk sample, which comes from the lattice damage caused by ion implantation. A significant increased backscattering yield can be clearly seen in thin-film sample. High backscatter yields are detected throughout the film that the lattice damage peak is no longer obvious, it can be seen more clearly in the enlarged image at the upper right corner. The experimental results show that unlike the local lattice disorder in bulk samples, C implantation causes a wider range of lattice distortion to the thin film. This result may be related to the lattice strain introduced by the implanted ions. For thin film crystals, the strain will cause deformation of the entire lattice, which can hardly be released by lattice relaxation.

The channel spectra of thin-film LiNbO₃ in as-implanted and suffering annealing at the temperature of 700 °C are shown in figure 3(a). As revealed by the figure the peaks around 423 channels increased significantly after annealing, which means the lattice structure of LiNbO₃ becomes more disordered near the surface. Compared with the results of our previous research, where part of C precipitated from C-implanted LiNbO₃ after 500 °C and 600 °C annealing [31], no trace of C was found on the surface of the present sample. A strong possibility for this phenomenon is attributed to the diffusion mechanism of C in LiNbO₃, which depends on not only the diffusion properties of C in LiNbO₃ but also the ion concentration. Obviously, the diffusion temperature of 500 °C for C in LiNbO₃ is much lower than that in metal Ni and Cu. Annealing at higher temperature accelerates the diffusion of C toward the crystal surface. However, when the concentration of ions reaches a certain value, that is, the distance between C ions is small enough, the aggregation of C becomes the
dominant. As a result, ions aggregate in the form of clusters and their diffusion behavior is severely inhibited. Since the cluster formation is driven by the outward diffusion, a bit like snowballing, the clusters eventually stay under the crystal surface as they cannot diffuse. Their accumulation will cause severe lattice disorder near the crystal surface. If this analysis is reasonable, it means that the diffusion capacity of C in LiNbO₃ will ultimately be reduced to zero, as there is no diffusion path for C ions driven by 700 °C annealing. This makes the precipitation of C on LiNbO₃ impossible. This result is consistent with the RBS results above.

X-ray diffraction (XRD) analyses were also carried out to characterize the lattice structure of LiNbO₃ samples, using CuKα radiation (40 kV and 40 mA), in increment of 0.02° with a counting time of 0.04 s for each step. Figures 3(a) and (b) are XRD spectra of thin-film LiNbO₃ crystal and bulk LiNbO₃ crystal under three conditions: original, as-implanted and post-implant annealing at 700 °C and 900 °C respectively. The strongest main diffraction peak comes from the (001) plane of the z-cut LiNbO₃. Although the intensity of the diffraction peak of bulk LiNbO₃ is several orders of magnitude higher than that of thin film LiNbO₃, the full width at half maximum (FWHM) indicates that both samples have very good crystallinity. Values of normalized peak intensity and FWHM of diffraction peak (0 0 6) of both samples at three cases are given in figures (c) and (d). It can be clearly seen that after implantation the peak values of both thin-film and bulk LiNbO₃ decrease and FWHMs increase, consistent with the result of degraded lattice structure induced by carbon implantation. Different from the usual understanding that high temperature annealing is beneficial to restore the lattice structure, the lattice damage induced by C implantation here is not improved with the annealing treatment for both film and bulk samples. Distortion of the lattice structure becomes solidified due to the intervention of the C cluster. This distortion can be exacerbated by the presence of larger sized clusters, which are likely to form at higher temperatures, just like the case of bulk sample in the present experiment. These XRD results are good consistent with the RBS results above.

In order to observe carbon distribution, the scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) mapping diagrams were made with the acceleration voltage of 15 kV, as shown in figures 5(a)–(d). Figure 5(a) is the SEM image of the sample surface of annealed bulk LiNbO₃ crystal, and (b)–(c) are EDS mapping diagrams of the C, Nb, O elements of the image (a), respectively. As can be seen in the figure, sample surface becomes rough after annealing and some long strips appear on the surface. By comparing the morphology of sample surface with the distribution of C, Nb and O, it can be clearly seen that these evenly distributed elements

![Figure 3](image-url)
do not match these stripes. Their appearance has nothing to do with the precipitation of C. The atomic force microscope (AFM) image of one strip is shown in figures 5(e)–(f). These bulged strips with a height of dozens of nanometers and a width of hundreds of nanometers may be the result of lattice deformation on sample surface, which often occurs on the annealed C-implanted LiNbO₃ crystal [32]. Our Raman measurement also ruled out the possibility that these bumps are related to C. Similar results have been obtained for SEM and EDS mapping images of thin-film LiNbO₃ crystal. Based on the above analysis, it can be concluded that the C signal in EDS here should come from the C cluster or aggregation in LiNbO₃ crystal near sample surface.

Since Raman spectroscopy is a commonly used method to characterize carbon materials, the excitation laser of Raman spectroscopy has a certain penetration depth, and some information near the surface of the material can usually be brought out.

After many attempts, the information of carbon below the surface of LiNbO₃ was detected by Raman spectroscopy with the excitation wavelength at 532 nm, the result is shown in figure 6. As shown in the figure, the detectable Raman signals are mainly distributed between 1200 cm⁻¹ and 3500 cm⁻¹. Except for an obvious peak at about 1577 cm⁻¹ (G peak), two faint peaks are located at number of 1421 cm⁻¹ (D peak) and 2840 cm⁻¹ (2D peak) respectively, and the G peak and the D peak are basically integrated, spanning from about 1250 cm⁻¹ to about 1750 cm⁻¹. The above Raman spectrum is similar to that of commercial activated carbon [33], which is composed of carbon quantum particles of inconsistent size and shape, and has extremely poor crystallinity. This result supports our analysis above. Because C concentration presents a Gaussian-like distribution along the implant path, particles formed by aggregation may not have a uniform size. In addition, the formation and growth of C clusters is done in a dynamic outward diffusion process, the size of C clusters was subject to the ion density and the local C diffusion capacity at the same time. This allows the formed cluster size to have a relatively large distribution range. The experimental results clearly show that it is essential to avoid the occurrence of C aggregation to achieve C precipitation out of the crystal. To do this, a more uniform C ion distribution and moderate annealing process should be taken into consideration.

4. Conclusions

Direct implantation of carbon ions into LiNbO₃ to produce graphene has become a new, potential and valuable research topic. In our experiment, thin-film LiNbO₃ crystal and bulk LiNbO₃ crystal of z-cut
were direct implanted by 30 keV C ions with a dose of $1.14 \times 10^{16} \text{ cm}^{-2}$ and then annealed at different temperatures, thin-film LiNbO$_3$ at 700 °C and bulk LiNbO$_3$ at 900 °C, respectively. The results of RBS and XRD show that the annealing fails to repair the damaged lattice, which in turn exacerbates the lattice disorder at surface. This result is in contrast to previous experimental reports on C implantation of transition metals followed by annealing and our experience on annealing of ion-implanted LiNbO$_3$.

Combining all the experimental results, it is reasonable to suppose that during annealing the out-diffusion and aggregation of C occur simultaneously. According to the EDS mapping and Raman spectrum, C finally accumulates near the inner surface of the LiNbO$_3$ crystal in the form of activated carbon. Carbon aggregation and failure of crystalline recovery of LiNbO$_3$ are not conducive to the direct production of graphene on LiNbO$_3$ crystal. However, the present experiment provides experience and reference for the experimental parameters of graphene production by direct C implantation into LiNbO$_3$. Research on the thermal behavior of carbon ions in LiNbO$_3$ also shows that to suppress the aggregation of C, reducing the density gradient of C and adopting a moderate annealing process may be a possible effective method. Further experiments are still in progress.

Figure 5. (a) SEM image of annealed bulk LiNbO$_3$ after ion implantation, (b)-(d) EDS mapping for C, Nb, and O elements in the region shown in (a), (e) AFM image of the strip in annealed bulk LiNbO$_3$, (f) AFM height profiles along the solid red line in (e).
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Figure 6. Raman spectrum of carbon material under and near the surface of annealed LiNbO₃ after ion implantation.
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