Effects of Annealing Temperature on Raman Scattering and Electrical Properties of Te-Doped Nanostructured Black Silicon

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Abstract

In this paper, the influence of annealing temperature on Raman scattering and transport properties of Te-doped nanostructured black silicon has been studied. We prepared the black silicon samples by wet etching, i.e. alkaline etching and metal assisted etching. The nanopores on the surface of black silicon were produced by metal assisted etching. The black silicon samples were annealed at different temperature of 600 °C, 700 °C, and 800 °C. According to the Raman scattering results, the peak intensity of Si increases with the increase of annealing temperature. However, the full width at half maximum (FWHM) is inversely proportion to the annealing temperature. Thermal annealing removes the Raman peak of amorphous Si at 480 cm⁻¹. In term of Te dopant atoms, the peak intensities of annealed samples are much lower than that of unannealed one. Subsequent Hall Effect measurement shows that annealing treatment improves electronic transport properties of Te-doped nanostructured black silicon.

Keywords: Raman scattering, annealing, nanostructured black silicon, Hall Effect measurement

1. Introduction

Nanostructured semiconductor owns great potential for achieving optical communication (Myers et al., 2006) and sensor net. Due to high absorbance (~90%) (Crouch et al., 2004) and wide absorption spectrum ranging from ultraviolet (UV) to near infrared (NIR) (Younkin et al., 2003; Das et al., 2012; Sheehy et al., 2005), nanostructured black silicon is an ideal material to fabricate sensitive photodetectors, solar cell (Yuan et al., 2009; Koynov et al., 2006), biochemical sensor (Noval et al., 2011), display devices (Treado et al., 1994; Tezcan et al., 2003; Fixe et al., 2004), gas sensor (Trakhtenberg et al., 2012). Nanostructure of the black silicon has been the focus of intense interest in recent years due to their extensive device application (Li et al., 2011; Li et al., 2008; Kumar et al., 2012). There are mainly four ways to fabricate black silicon-femtosecond laser (Wu et al., 2001; Kabashin et al., 2010; Othonos et al., 2009), deep reactive ion etch (DRIE) (Fischer et al., 2009), metal assisted wet etching (Branz et al., 2009), and electrochemical etching (Ma et al., 2006). Eric Mazur (Crouch et al., 2004) microstructured silicon surfaces with femtosecond laser irradiation in the presence of SF₆. The sulfur element was introduced into silicon in the ablation process so as to introduce states into the band gap of crystalline silicon and thus enhance the below-band gap absorption. For this reason, silicon doped with Te was chosen for the fabrication of black silicon. In this work, the nanostructured black silicon was fabricated by wet etching method. The single crystal silicon was immersed in a solution containing hydrofluoric acid (HF) and hydrogen peroxide (H₂O₂). The crystal silicon is etched in the presence of noble metal catalysts (Nishioka et al., 2008).

Thermal annealing is widely used in modern silicon device manufacturing technology. It is a thermal processing technique with isothermal annealing behavior and leads to a uniform lateral and transverse heating profile throughout a wide area.

In this work, the effects of annealing temperature on Te diffusion and electrical properties of nanostructured black silicon photodetector was investigated by Raman scattering and Hall Effect measurement. Raman scattering provides a fast and non-destructive way to determine the degree of crystallization and tensile/compressive stress from the peak shape and peak position (Choi et al., 1999; Nesheva et al., 2002). Furthermore, Subsequent Hall Effect measurement shows that annealing at different temperature has a
significant influence on the electronic properties of Te-doped nanostructured black silicon, such as mobility, conductivity, and sheet concentration.

2. Experiment

Figure 1 shows the fabrication process of black silicon by wet etching. Te doped silicon was obtained by ion implantation of Te into single crystal silicon (100) wafer ($R=8 \ \Omega/cm^2$) at applied voltage of 40 kV, resulting in a bulk concentration of $1 \times 10^{16} \ cm^{-3}$. According to the TRIM98 ion implantation simulation, the depth of Te dopant atoms is about 74.2 nm with a peak density at 27.8 nm. As shown in Figure 1, firstly, $Si_3N_4$ pattern was obtained on the surface of silicon by PECVD and lithography. Secondly, the Te-doped Si wafer padded by $Si_3N_4$ as mask was etched by alkaline solution (5g KOH+10mL deionized water+15mL isopropanol) in the Constant Temperature Water-bathing at temperature of 50°C, forming the micro-column columns, as shown in Figure 1(b). The Te-doped Si wafer was immersed in HAuCl$_4$, H$_2$O$_2$, HF (Volume rate=1: 7: 5) mixed reactive solution for 8 min at room temperature. As shown in Figure 1(c), the Au nanoparticles from HAuCl$_4$ facilitate the etching in HF and H$_2$O$_2$ (Li et al., 2000) and fabricate the porous structure on the surface. Consequently, black silicon material is produced. Figure 2 presents the SEM images of nanostructure achieved by Au assisted HF/H$_2$O$_2$ etching. Figure 2(a) and Figure 2(b) exhibit the top view and cross-section view of nanopores on the surface of black silicon, respectively. The diameters of the nanopores range from 60 nm to 100 nm and the depth of etched nanopores is larger than 500 nm. The high aspect ratio of these nanopores enhances the absorption of black silicon remarkably.

After fabrication, three samples were quickly annealed for 1 hour at pressure of $3.6 \times 10^{-3} \ Pa$ by furnace annealing at temperature of 600°C, 700°C, and 800°C, respectively. An unannealed sample was used as control sample in our experiment.

![Figure 1. Schematic diagram of fabrication of Te-doped nanostructured black silicon: (a) Te-doped Single crystalline silicon padded with $Si_3N_4$ as mask; (b) Micro-column structure after anisotropic KOH etching; (c) nanopores achieved by metal-assisted wet etching](image-url)
Figure 2. SEM images of nanostructure after HF/H2O2 etching: (a) top view of nanopores; (b) the cross-section view of nanopores

The influence of annealing temperature on the crystal and chemical properties of the nanostructured black silicon layer were analyzed with JY-HR800 Raman scattering system. In Raman scattering measurement, the wavelength of laser is 532 nm and power is 1 mW. Meanwhile, the electrical properties of unannealed and annealed black silicon samples were characterized by Hall Effect measurement.

3. Results and Discussion

3.1 Raman Scattering Results of Annealed Black Silicon

Figure 3 shows the room temperature Raman scattering spectra of the samples after thermal annealing treatment at different temperatures. As exhibited in Figure 3, the Si nanocrystal Raman peaks are observed in 521 – 522 cm\(^{-1}\) range for all samples. The intensity is proportional to the annealing temperature. The Raman spectrum of nanocrystals on the surface of black silicon at different annealing temperature is asymmetric due to photon confinement.

Table 1 exhibits that the measured normalized Raman intensity (\(I_\beta\)), peak position (\(\omega\)), FWHM, and average nanocrystal size (\(d\)), of black silicon for different annealing temperature (\(T_a\)), in Figure 3. It is noteworthy that the calculated Raman line shape depends very critically on the size of the nanocrystal. The mean size of nanocrystal measured by high resolution electron microscopy (HREM) increases with increasing annealing temperature. This is attributed to that the higher annealing temperature causes less grain boundaries in the film, and the film will become more crystalline. The similar peak position for all sample suggests that when nanocrystal semiconductor were etched to a reasonable size (Choi et al., 1999), varying annealing temperature does not shift the peak position and the peak position should get closer to that of the bulk Si value of 521 cm\(^{-1}\).
Table 1. Measured Raman peak positions $\omega$, FWHMs, mean sizes of nanocrystallites, $d$, and normalized intensities, $I_R$, at different annealing temperature

<table>
<thead>
<tr>
<th>$T_a$ (°C)</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$I_R$ (%)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>521.3</td>
<td>52.6</td>
<td>4.4</td>
<td>3.2</td>
</tr>
<tr>
<td>600</td>
<td>521.3</td>
<td>53.2</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>700</td>
<td>521.3</td>
<td>95.3</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>800</td>
<td>521.3</td>
<td>100</td>
<td>2.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>

In Figure 3, the first peak intensity of Si, at the wave number of 521.3 cm$^{-1}$, increases proportionally to annealing temperature. The peak intensity of Si of annealed samples is higher than that of unannealed one. This is due to that high temperature thermal annealing was reported to be able to release the stress and decrease the structure faults (Zacharias et al., 1999). The vacancies near the film-substrate interface appear restructured after annealing treatment. It is possibly influenced by growth defects near the interface. However, the defects in the nanostructured black silicon are partially removed in the deeper of film (Reurings et al., 2010). In addition, the Te dopant atoms were forced to diffuse into deeper of silicon film in the annealing process, which accelerates the Raman scattering efficiency between Si atoms and incident light on the surface of black silicon. For these two reasons, the Raman intensity of Si at 521.3 cm$^{-1}$ increases with increasing annealing temperature. On the other hand, the full width at half maximum (FWHM) of samples annealed at 600°C, 700°C, and 800°C is 3.4 cm$^{-1}$, 2.9 cm$^{-1}$, and 2.1 cm$^{-1}$, respectively, as indicated in Table 1. However, the FWHM of unannealed sample is 4.4 cm$^{-1}$. The decrease of FWHM results from the thermal annealing process which increases the crystallinity of black silicon.

![Figure 3. Raman scattering results of Te-doped nanostructured black silicon annealed at different temperature: (a) unannealed; (b) 600°C; (c) 700°C; (d) 800°C](image-url)
Since the strong Raman peak from the crystalline Si substrate masked the peak of ion implanted Te, the large Si peak intensity was ignored in order to observe signal from Te in the low intensity range as shown in Figure 4. The Raman peaks of Te doped black silicon are presented at the wave numbers of 123 cm\(^{-1}\) and 143 cm\(^{-1}\). It is worthwhile to note that the peak intensities of annealed samples are much lower than that of the control sample. However, as for the annealed samples, the intensities at these two wave numbers are enhanced by increasing the annealing temperature. This is mainly ascribed to that annealing treatment boosts the diffusion of ion implanted Te atoms deeper into the nanostructured black silicon layer and thus reduces the sheet concentration of Te atoms at relative low temperature. Furthermore, the lower annealing temperature process does not provide sufficient energy to remove defects or vacancies. For these two reasons above, peak intensities of Te for the annealed samples are low. Nevertheless, as the annealing temperature increases, the point defects surrounding Te atom induced by ion-implantation were eliminated during the thermal process. Due to the decreasing concentration of defects, the Raman scattering efficiency between Te atom and incident light was enhanced, leading to increase of Raman peak intensity of Te for the annealed samples.

As shown from Figure 4, a Raman peak at the lower frequency side of Si peak appears at 477 cm\(^{-1}\). It was only observed for the unannealed sample. Its FWHM is larger than that of the Si peak at 521 cm\(^{-1}\) which is similar to the characterized scattering band of amorphous Si at 480 cm\(^{-1}\). However, for the annealed samples, there is no peak observed at the wave number from 470 cm\(^{-1}\) to 480 cm\(^{-1}\) in Figure 4. It implies that the ion implantation and sequent wet etching introduces lattice defects, dislocations and vacancies in the nanostructured black silicon. The high temperature annealing process is able to restructure the vacancies near the black silicon-single crystal silicon interface and remove the ion implantation induced defects. The elimination of lattice defects, dislocation and vacancies decreases the amount of amorphous Si in the film and therefore reduces Raman scattering intensity at the amorphous Si peak of 480 cm\(^{-1}\).

3.2 Hall Effect Measurement of Annealed Black Silicon

Table 2 shows the electric properties of nanostructured black silicon samples by Hall Effect measurement. The sign of Hall voltage is positive. The majority carriers in the nanoporous layer are holes. The intensity of magnetic field is 0.36 T in the Hall effect measurement. In Table 2, \(N_h\) is carrier concentration, \(\mu\) is Mobility, \(\rho\) is Resistivity, and \(\sigma\) is Conductivity for nanopores, respectively.

In Table 2, the mobilities of the annealed samples are much larger than the one without annealing. The highest mobility value is \(3.6\times10^4\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) at the temperature of 700°C. This is mainly attributed to the thermal treatment process reduces tensile stress and point defects on Si nanocrystals. And thus, the lowest concentrations of deactivating defects and limitation of the formation of point defects are produced by migration process during the cooling down (Gaiduk et al., 2003). Elimination of deactivating defects and point defects decreases the scattering efficiency of carriers and thus improves the mobility in the nanostructured black silicon. On the other hand, due to the annealing process accelerates the Te dopants diffusing into deeper of black silicon, the higher
concentration of Te atoms will lower the drift speed of carriers under electric field. For this reason, the mobility at 800°C is lower than that of sample annealed at 700°C. Since the high temperature annealing in vacuum accelerates the diffusion of Te dopant and motivates the doped atoms diffuse deeper into the black silicon, the number of donor carriers contributed by ion implanted Te atoms is enhanced. And then, the additional electrons from dopant atoms is released to enhance the free-carrier concentration (Carey et al., 2005). In terms of bulk concentration indicated in Table 2, the carrier concentration of black silicon sample annealed at 600°C 700°C, and 800°C is 8.7×1014 cm-3, 1.1×1015 cm-3, and 3.8×1016 cm-3, respectively. However, the carrier concentration for unannealed sample is 2.8×1014 cm-3.

With regards to the conductivity, due to the increase of mobility and bulk concentration upon annealing temperature, the conductivity increases proportionally to the annealing temperature significantly. The conductivity of control sample is only 5.8×10⁻³ Ω⁻¹. However, the conductivities of annealed ones are at least one order of magnitude greater than the one without annealing.

Table 2. Hall Effect results of black silicon samples annealed at 600°C, 700°C, 800°C, and without annealing, respectively

<table>
<thead>
<tr>
<th>Ta (°C)</th>
<th>N_b (cm⁻³)</th>
<th>µ (cm²/Vs)</th>
<th>ρ (Ωcm)</th>
<th>σ (1/Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unannealed</td>
<td>2.8×10¹⁴</td>
<td>1.3×10⁷</td>
<td>1.7×10⁴</td>
<td>5.8×10⁻³</td>
</tr>
<tr>
<td>600</td>
<td>8.7×10¹⁴</td>
<td>8.4×10⁵</td>
<td>8.3×10⁰</td>
<td>1.2×10⁻¹</td>
</tr>
<tr>
<td>700</td>
<td>1.1×10¹⁵</td>
<td>3.6×10⁴</td>
<td>1.6×10⁻¹</td>
<td>6.3×10⁰</td>
</tr>
<tr>
<td>800</td>
<td>3.8×10¹⁶</td>
<td>4.1×10⁵</td>
<td>4.0×10⁻²</td>
<td>2.5×10¹</td>
</tr>
</tbody>
</table>

4. Conclusion

The temperature of annealing is a key factor that affects shape and intensity of Raman spectroscopy of Te-doped nanostructured black silicon. According to the Raman scattering measurement, the Raman peak intensity of Si at 521.3 cm⁻¹ upgrades with increasing annealing temperature significantly. However, the FWHM of annealed sample at Si peak is lower than that of unannealed one and decreases with increase of annealing temperature. Thermal annealing increases the crystallinity of black silicon and reduces the concentration of point defects and vacancies. Therefore, it is demonstrated the disappearance of amorphous Si peak at 477 cm⁻¹ caused by heat treatment. The Raman scattering intensity of Te increases with increasing annealing temperature but is smaller than that of unannealed sample. Hall effect measurement indicates that thermal annealing process boosts the dopant diffusion and electrical properties of nanostructured black silicon material. The electrical properties, such as mobility, resistivity, carrier concentration, were changed by orders of magnitude during thermal annealing process because the stress and point defects in the nanostructured black silicon were eliminated.

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