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Photoluminescence detection of oxygen in carbon-implanted electron-irradiated silicon crystal

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Photoluminescence (PL) from radiative centers produced in silicon crystal by carbon ion implantation and high-energy electron irradiation has been studied. From the PL intensity of the 0.79 eV carbon oxygen complex formed by the carbon implantation, oxygen can be easily detected in a thin silicon crystal which does not contain a considerable level of carbon. The carbon dose, annealing conditions and electron irradiation dose yielding the highest sensitivity for detection of the oxygen are reported.

1. INTRODUCTION

Oxygen is the main impurity in crystalline silicon, and it has been extensively studied because of its influence on the mechanical and electrical properties of silicon. A certain amount of oxygen in the crystal promotes mechanical strength and forms oxygen microprecipitates which are useful in gettering metal contaminants(1). Due to reduced physical dimensions and intolerance to contaminants in LSI processing, it is, and will increasingly become, important to accurately measure and control the concentrations of oxygen in thin silicon layers.

The usual method for measurement of oxygen in bulk silicon is using the local mode infrared absorption peak at 1106 cm^{-1} due to interstitial oxygen(2). This method, however, requires a long path length of several millimeters to observe $10^{16}/cm^3$ levels of oxygen owing to the low absorption coefficient of the vibration species.

In this report, the possibility of detecting low levels of oxygen in silicon wafers is studied via photoluminescence (PL) spectra of the carbon oxygen complex which appear at 0.79 eV(0.79eV defect). The complex is formed by carbon ion implantation, thermal annealing, and electron irradiation of a sample. In principle, when a crystal contains both oxygen and carbon, this technique has high depth sensitivity, on the order of 10 μm(3), and is known to be sensitive to atomic concentrations on the order of $10^{15}/cm^3$(4).

2. EXPERIMENTAL

The oxygen concentration in the samples was $8x10^{17}/cm^3$. The content of the carbon in the crystal was confirmed to be lower than $1x10^{15}/cm^3$ by charged particle activation analysis. The carbon ion implantation was performed using CF_4 source gas in a magnetron rf implanter at 50 keV acceleration. The dose range of carbon was from $10^{13}ions/cm^2$ to $10^{16}ions/cm^2$. The annealing temperature was 800°C to 1150 °C for duration's of 0.5, 7 and 30 hours.

The samples were irradiated by 1 MeV electrons with doses from $1x10^{14}/cm^2$ to $4x10^{17}/cm^2$ at the Takasaki Radiation Chemistry Establishment of Japan Atomic Research Institute.

The PL measurements were performed in a standard luminescence setup. The samples were maintained in a liquid-helium-cooled cryostat. The excitation light was the 488 nm Ar ion laser line at a laser output power of 100 mW. The luminescence light was dispersed by a monochromator, a liquid nitrogen-cooled Ge detector detected the light, and a lock-in amplifier processed the signal.

3. RESULTS AND DISCUSSION

We successfully observed strong PL peaks due to C_i-O_i and C_s-Si_i-C_s complexes for samples prepared by carbon implantation, thermal annealing, and electron irradiation. A typical PL spectrum is shown in Fig.1. This spectrum is the same as that obtained from the crystal containing both carbon and oxygen(3) after electron irradiation. Two sharp and strong peaks can be seen at 0.79eV and 0.969eV, which are zero-phonon replicas of the C_iO_i and C_s-Si_i-C_s complexes, respectively(5). A small TO phonon replica peak related to the 0.969eV defect appears at 0.898eV.

The PL peak intensity is closely related to carbon doses, annealing conditions, and electron irradiation doses. When there was no carbon implantation, we could not observe any peak due to carbon-oxygen complexes, even with electron irradiation, because of the absence of carbon impurity in the initial crystal.

Since the aim of this study is to detect oxygen in silicon crystal, only the 0.79eV defect is discussed. First, we considered the effect of electron doses on the PL intensity. The PL peak intensity increases strongly with electron dose, from no observable peak at $10^{14}e^-/cm^2$ to an intense peak between $10^{16}e^-/cm^2$ and $10^{17}e^-/cm^2$ for carbon doses of $10^{13}/cm^2$ and $10^{15}/cm^2$ and annealing at 1000°C for 30 hours. However, the peak intensity for unannealed samples is generally lower compared to the high temperature annealed samples and it does not show any remarkable increase, even after high electron doses of $1x10^{17}e^-/cm^2$, indicating that the PL intensity is much influenced by the crystallinity of the ion implanted region of the crystal.

The crystallinity of the implanted region can be examined by Raman spectroscopy(6). Raman scattering intensity of the lattice vibration (TO phonon) decreases with increased ion doses.

Next, we examined the influence of the carbon doses on the PL peak intensity for samples electron irradiated with $1x10^{17}e^-/cm^2$ and annealed at 1000°C for 30 hours. The PL intensities of the 0.79eV defect of samples with the carbon doses from $1x10^{13}/cm^2$ to $1x10^{15}/cm^2$ are very large, among these the sample with the dose of $1x10^{14}/cm^2$ is the largest. The PL intensity of the sample implanted with $1x10^{16}/cm^2$ of carbon is very small compared to those of the other samples. This is caused by degradation of the crystallinity of the heavily implanted sample. From transmission electron microscopy (TEM), we confirmed that the crystallinity of the implanted region of this sample becomes amorphous after the carbon implantation, and it becomes poly-crystalline after annealing at high temperatures. In order to detect oxygen atoms in silicon crystals with high sensitivity, therefore, higher dose implantation of carbon than $1x10^{16}/cm^2$ should be avoided.

The annealing conditions also influence the PL intensity through the crystallinity of the implanted region of the carbon. Since implantation defects such as W and X centers remain in the crystals annealed at lower temperatures than 600°C(7), we employed annealing temperatures higher than 800°C in this study. For carbon doses from $10^{13}/cm^2$ to $10^{15}/cm^2$, the PL intensities increase between the 800 and 1000°C annealings and are nearly the same between the 1000 and 1150°C annealings. However, the intensities for samples with a carbon dose of $10^{13}/cm^2$ and annealing above 1000°C drop irrespective of annealing time. In general, however, increasing the annealing time has a positive effect on the PL intensity. Accordingly, it is appropriate to employ temperatures between 1000 and 1150°C for several hours for annealing of implanted crystals.

The best conditions for the PL detection of oxygen in silicon crystal containing little carbon, using carbon-implantation electron -irradiation technique are summarized as: carbon implantation with doses from $10^{13}/cm^2$ to $10^{15}/cm^2$, annealing temperatures from 1000°C to 1150°C for several hours, and electron irradiation doses from $10^{16}/cm^2$ to $10^{17}/cm^2$.

Depth profiles of carbon measured by SIMS for unannealed and annealed samples of $10^{16}/cm^2$ carbon dose before irradiation are shown in Fig.2. The annealed samples have a slightly lower carbon peak intensity than the unannealed sample. The profiles for both unannealed and annealed samples have almost the same shape and width. As the projected range is 110nm and the diffusion does not occur in a long range, most carbon remains within a region of less than several μm, 10μm at most.

From the value of the signal to noise ratio(S/N) of the 0.79eV peak shown in Fig.1, we estimated the detection limit of oxygen. The S/N value is 500 for the sample with oxygen content of $8x10^{17}atoms/cm^3$, carbon implantation of $1x10^{14}/cm^2$, annealed at 1000°C for 3 hours, and electron irradiation of $1x10^{17}e^-/cm^2$. This value indicates to us the possibility of detecting oxygen concentration as low as about $5x10^{15}atoms/cm^3$ in a thin film of several μm thickness.

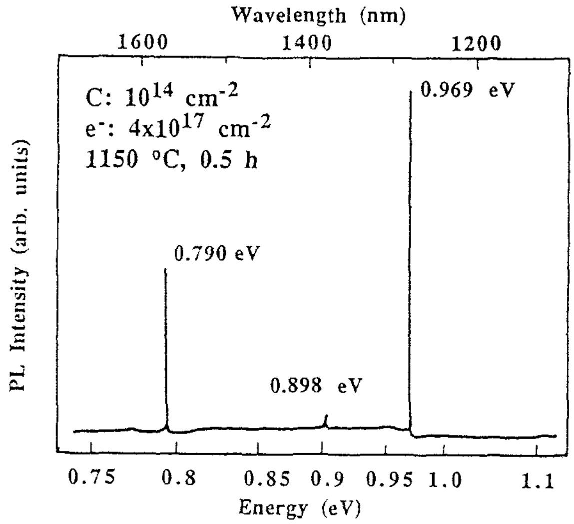

Fig. 1 PL spectrum of carbon implanted, thermal annealed, electron beam irradiated silicon crystal.

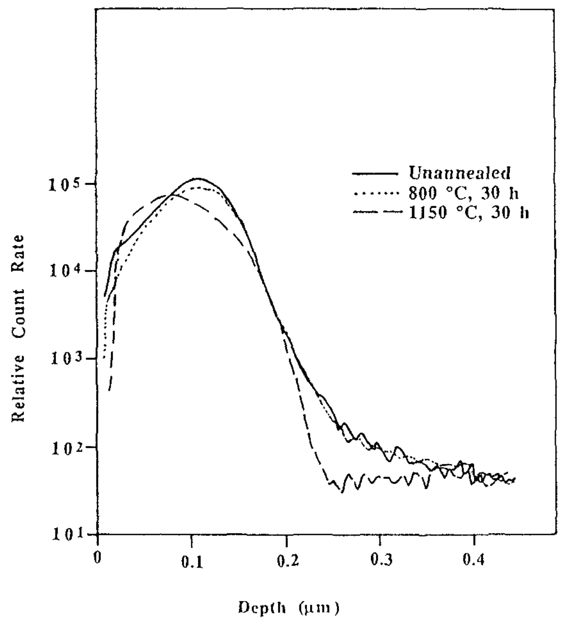

Fig. 2 SIMS depth profile of carbon for 10^{16} /cm^2 carbon-implanted sample before and after annealing.

4. CONCLUSION

The possibility of detecting oxygen in carbon-implanted electron-irradiated silicon crystal by photoluminescence (PL) has been studied. This technique was seen to be an promising method for detecting low levels of oxygen in silicon. The PL results indicated that luminescent complex production depends on preparation conditions. For the range of preparation conditions used in this study, the optimum conditions to detect low levels of oxygen in crystal are: carbon dose from 10^{13}/cm^2 to 10^{15}/cm^2, annealing between 1000°C and 1150°C for several hours, electron dose of $10^{17}e^-$/cm^2. The possibility was seen for detecting oxygen concentration as low as about $5x10^{15}$atoms/cm^3 in thin silicon film of several μm thickness

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