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Determination of Oxygen Concentration in Heavily Doped Silicon Wafer by Laser Induced Breakdown Spectroscopy

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Abstract: Laser-induced breakdown spectroscopy (LIBS) has been applied to determine the oxygen concentration in heavily doped silicon wafer by using a high power pulsed laser and an optical fibre coupled CCD spctrometer. The relative concentration of oxygen in the heavily doped silicon wafer was calculated by the ratio of the integral intensity of the O_I emission of oxygen to the SiI emission silicon from the LIBS spectra. A calibration curve was obtained by comparing the oxygen concentration determined by LIBS with the oxygen concentration determined by conventional FTIR technique used in Si industies, in which a set of four lightly doped CZ silicon wafers were used. Based on the calibration curve, quantitative oxygen concentration in several heavily doped silicon samples was measured.

Key words: LIBS; oxygen concentration; heavily doped silicon

Oxygen is one of the most important impurities in single crystalline silicon, and it has great influences on the electrical and mechanical properties of silicon[1-3]. In the IC processes, oxygen induced defects and/or oxygen complexes which act as thermal donors and recombination centers result in the short minority carrier lifetime and higher leakage current[4]. Furthermore, dislocations caused by oxygen presipitations will reduce the mechanical strength of silicon wafer[5-6]. On the other hand, oxygen has positive effects in IC processes, and is commonly used to deliminate most detrimental metal elements in the active region of a device, *i.e*., the so called internal gettering technique[7-8]. Thus, it's a significant work either to measure or control the oxygen concentration in silicon.

Fourier transform infrared (FTIR) spectrometer is a routine and standard technique for the determination of oxygen concentration in silicon wafers[9-10]. But unfortunately, FTIR is not suitable for the heavily doped silicon wafers, because of the strong free-carrier absorption which hide the weak infrared absorption of Si–O–Si. Besides, secondary ion mass spectrometry (SIMS)[11] and gas fusion analysis (GFA)[6] can both measure the oxygen concentration in silicon, but these methods are destructive in nature, complex in instrumentation, or/and expensive in equipments.

Nowadays, as a brand new analysis technique of composition and trace elements analysis, laser induced breakdown spectroscopy (LIBS) is studied widely for solids[12-13], liquids[14-15], and even gaseous materials[16-17]. It uses high power laser pluses to irradiate the sample, and the high temperature produced by the the irradiation of laser on sample surface results in the formation of plasma. Excited atoms and ions in the plasma emit characteristic emission lines during the de-excitation processes. Thus the elements in the sample can be readily determined by anlyzing the emission spectra emitted from the plasma. LIBS has many advantages, such as simple in instrumentation, it is fast enough to do real-time and *in situ* analysis if a CCD spectrometer is used; it's capable of analyzing all elements with high sensitivity; and it does not require complicated sample preparation[18-19]; it can analyze solid, liquids, and gases; it only needs a small area for the analysis of the sample since the laser spot is very small, which means that the wafer is reusable. For the analysis of oxygen in silicon, LIBS technique is not interfered by the strong free carrier absorption, as that ocuured in FTIR analysis. All these

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merits indicate that LIBS is a very useful technique in semiconductor industry, especially for heavily doped silicon.

Most previous LIBS measurements have used a complicated synchronous accessory between the laser and the conventional diffraction grating based spectrometer which act as the detector[20]. Instead, a spectrometer with a linear CCD is used as the detector, which acquire data simutaneously for all wavelengths. Thus the effect of the shot to shot variations of laser power on the signal intensity could be greatly reduced, and the signal to noise (S/N) ratio of the LIBS spectra could be greatly improved.

1 Experimental

The schematic diagram of the LIBS system is as shown in Fig. 1. Laser beam is focused by a lens set and hits the sample through a quartz viewport, which results in very high temperature and produces plasma near the sample surface. The emission from the plasma is focused by another lens set and then collected by the spectrometer (Ocean Optics HR4000) *via* an optical fiber, and then the collected spectra is stored and displayed in a PC. The high power pulsed laser used in this paper is a Nd:YAG laser (ZKLASER, MQV-2000-10, pulse width of 8ns, maximum pulsed power of 2000mJ, repetition rate of 3–10Hz, four selectable wavelength at 1064, 532 and 355nm, and 266nm). In this paper, wavelength was set to 532nm, and pulsed power was set to 1200mJ, and the repetition rate was set to 10Hz. The sample was mounted on a micro-goniometer stage allowing positional adjustment and at an incidence angle of 45 degree to the laser beam. Samples were placed in a vacuum chamber in order to get rid of oxygen in air.

To quantitatively analyze the oxygen concentration in Si wafer, a calibration curve is necessary. O_I emission (777.194, 777.417 and 777.539nm) and Si_I emission (288.159nm) lines were chosen for the intensity measurement according to the NIST Atomic Spectra Database[21]. The calibration curve is obtained by comparing the peak intensity ratio of O_I and Si_I emission intensity with the oxygen concentration determined by infrared absorption spectra of the same set of commercial CZ Si samples (samples 1#-4#).

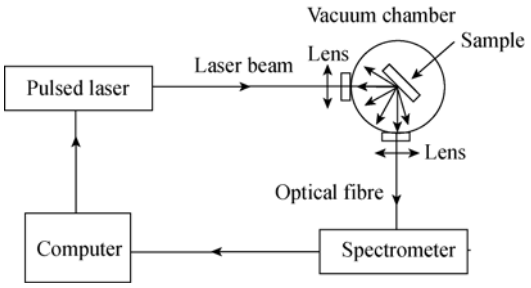

Fig. 1 Schematic diagram of the LIBS apparatus

2 Results and discussions

The infrared absorption spectra of the calibration set are shown in Fig. 2 in the range of 1100–1300cm^{-1}. The LIBS spectra of O_I and Si_I of the same set of samples are shown in Fig. 3. Due to the limited resolution of the spectrometer, the three lines of O_I are not well resolved, but this does not affect the mesurement of the peak intensity. The oxygen concentration N_O is calculated according to the method described by ASTM F723-88. The results are as shown in Table 1. According to the data of Table 1, the calibration curve is obtained as shown in Fig. 4 *via* the linear fit of the four data points.

The fitting of the data in Fig. 4 gives the equation:

$$N_O=21.54R-0.1445 \quad (1)$$

Where R is the intensity ratio of O_I/Si_I, and N_O is the oxygen concentration in the unit of 10^{16}cm^{-3} determined by FTIR.

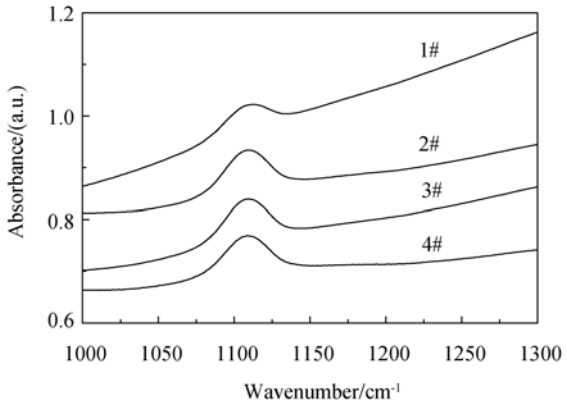

Fig. 2 Infrared absorption spectra of the set samples

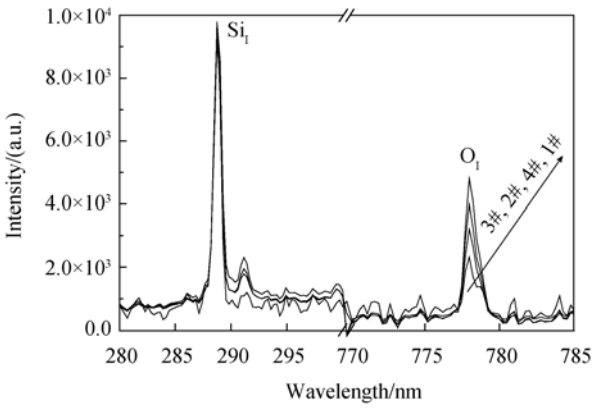

Fig. 3 LIBS spectra of the set samples

Table 1 The results of FTIR and LIBS of the samples 1#-4#

Sample	Thickness/μm	N_O/(×10^{16}, cm^{-3})	I_O/I_{Si} of LIBS
1#	332	9.55	0.451
2#	583	5.04	0.229
3#	739	3.59	0.194
4#	354	6.86	0.331

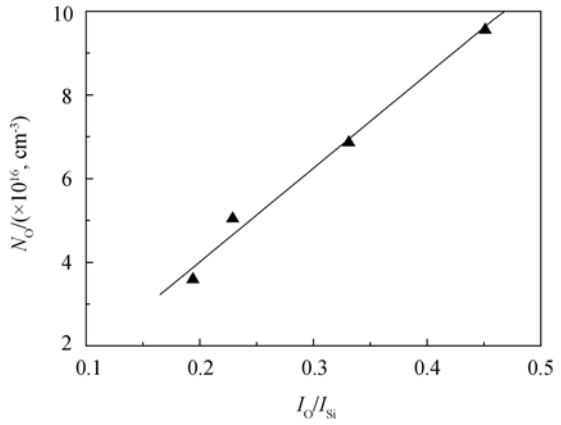

Fig. 4 Calibration curve obtained through samples 1#-4#

Figure 5 is the LIBS spectra of three heavily doped silicon samples (#5, #6, #7) cut from the same ingot of CZ silicon including at the shoulder, at the middle of the body, and at the tail of the Si ingot, respectively. The O_I/Si_I ratio calculated from LIBS signal are 0.355, 0.219 and 0.231, respectively for sample 5#, 6#, and 7#. Finally, the oxygen concentrations for the above three samples are 7.48×10^{16}cm^{-3}, 4.44×10^{16}cm^{-3}, and 4.70×10^{16}cm^{-3}, respectively, as determined by the calibration equation N_O=21.54R–0.1445. The trend of the change of oxygen concentration along the ingot axis determined by LIBS is similar to that of normally doped CZ silicon[6,22].

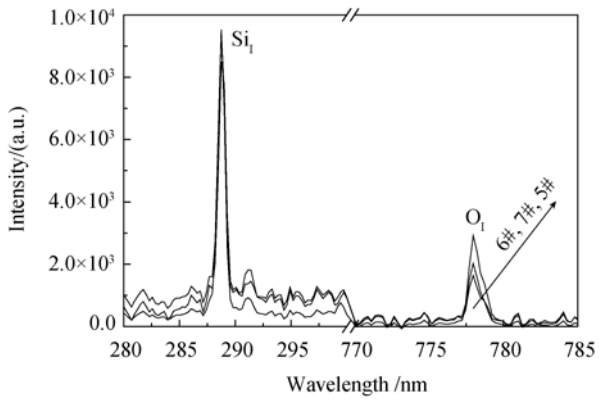

Fig. 5 Laser induced breakdown spectra of samples 5#-7# (Si_I at 288nm and O_I at 777nm)

3 Conclusions

In this paper, oxygen concentration in heavily doped silicon wafer was characterized by laser induce brakdown spectroscopy. A calibration curve was obtained between the oxygen concentration and the relative intensity ratio of I_O/I_{Si} in LIBS. Using this calibration curve, oxygen concentration in heavily doped CZ silicon were measured. The results show that LIBS is a powerful technique for the analysis of impurities in semiconductor materials, especially in areas in which conventional techniques fails, such as oxygen concentration in heavily doped silicon.

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激光诱导击穿光谱测量重掺硅中的氧含量

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摘 要: 利用一台高能脉冲激光器和一个光纤耦合的CCD光谱仪构建了激光诱导击穿光谱仪(LIBS), 并用它测量了重掺硅片中的氧含量. 硅中的氧含量通过LIBS谱中的O_I(777nm)谱线和Si_I(288nm)谱线的强度比值O_I/Si_I获得. 为了确定氧含量的绝对值, 选定了 4 个轻掺杂的硅样品, 分别利用业界通用的傅利叶变换红外吸收光谱(FTIR)和LIBS对其中的氧含量进行了测量, 由此得出了利用LIBS确定硅中氧含量的定标曲线, 并根据该定标曲线成功地测出了几个重掺硅片中的氧含量.

关 键 词: 激光诱导击穿光谱; 氧含量; 重掺硅

中图分类号: TB9 **文献标识码:** A