INTRINSIC GETTERING OF NICKEL IMPURITY DEEP LEVELS IN SILICON SUBSTRATE

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Abstract

The intrinsic gettering of nickel impurity in p-type silicon substrate has been investigated. The density of electrically active nickel in intentionally contaminated silicon was determined before and after oxygen precipitation by means of resistivity measurements. These data, coupled with minority carrier lifetime and infrared absorption spectroscopy measurements showed that apart from generating deep levels, nickel also acts as donor impurity and oxygen precipitates provided effective gettering sites for these impurities.

Keywords: intrinsic gettering, nickel impurity, oxygen precipitate, resistivity.

1. Introduction

Gettering techniques to remove harmful impurities from active device regions have now become an integral part of manufacturing silicon integrated circuits. Transition metal elements are the most prevalent of these unwanted impurities. They may be present in the as-grown silicon substrate as inherent impurities or inadvertently introduced during wafer cleaning or high temperature processing. These contaminants diffuse interstitially in silicon and ultimately degrade device performance by introducing multiple deep levels which act as traps or recombination centers. Nickel belongs to this class of impurities. The properties of nickel in silicon have been investigated by a number of researchers (Weber, 1983; Yoshida and Saito, 1967; Milnes, 1973; Graff and Pieper, 1981; Pearton and Tavendale, 1983; Lemke, 1987; Kitagawa and Nakashima, 1989; Kitagawa *et al.*, 1991; Tanaka *et al.*, 1996; Indusekhar and Kumar, 1987; Gong and You, 1989; Seibt and Schroter, 1989; Shen *et al.*, 1996; Ourmazd and Schroter, 1984). With regard to the diffusion property, nickel is known to be one of the fastest diffusing elements in silicon (Weber, 1983). It diffuses interstitially and precipitates or stays on electrically inactively sites (Yoshida and Saito, 1967), and only about one in every thousand of diffusing atoms remains in the electrically active substitutional sites (Yoshida and Saito, 1967). There has been some considerable discrepancy between researchers, however, on the electrical activity as well as the nickel-related deep levels in the silicon substrate. In the early years, based on Hall effect

and conductivity measurements, it was generally accepted that nickel introduced only acceptor levels around $E_c-0.35eV$ and $E_v+0.23eV$ in Si (Milnes, 1973). Later, based on deep level transient spectroscopy (DLTS) measurements, many more Ni-related deep levels were observed (Graff and Pieper, 1981; Pearton and Tavendale, 1983; Lemke, 1987; Kitagawa and Nakashima, 1989; Kitagawa *et al.*, 1991). While Graff and Pieper (1981) observed only one donor level at $E_v+0.15eV$, Pearton and Tavendale (1983) reported three levels all acceptors, at $E_v+0.18eV$, $E_v+0.21eV$ and $E_v+0.33eV$ due to nickel in p-type substrate. In 1987, Lemke reported one acceptor and donor level at $E_c0.38eV$ and $E_v+0.17eV$ respectively in nickel doped silicon substrates. Recently, Kitagawa and Nakashima (1989) and Kitagawa et al (1991) showed that nickel introduced amphoteric donor and acceptor levels at $E_v+0.18eV$ and $Ec+0.47$ respectively in silicon. More recently, Tanaka et al (1996) measured the capture cross section of the amphoteric Ni centers in silicon. On the contrary, there are reports (Indusekhar and Kumar, 1987; Gong and You, 1989) that Ni does not introduce any level, or Ni is electrically inactive in silicon. Some researchers (Seibt and Schroter, 1989; Shen *et al.*, 1996) have studied the precipitation behaviour of Ni in silicon crystals with little or no extended characterized defects. Their results showed that a high density of Ni precipitation is observed in a fast cooled specimen. Ourmazd and Schroter (1984) have studied the microstructural changes brought about by the intrinsic gettering of nickel

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during a two-step gettering anneal in silicon by means of High Resolution Transmission Electron Microscopy (HRTEM). Their results indicated that gettering proceeded by the emission of Si interstitials due to oxygen precipitation and the production of nickel silicide ($NiSi_2$) at the Si/SiO_2 interface. In this work, we have studied the intrinsic gettering of nickel in silicon under a three-step gettering anneal by means of resistivity, minority carrier lifetime and infrared absorption spectroscopy measurements.

2. Experimental

Boron doped Cz grown silicon wafer with a nominal resistivity of 5 ohm-cm was used for our investigation. The interstitial oxygen, O_i, and substitutional carbon, C_s, concentrations in the (100) oriented wafer, determined by infrared measurements are 1.1×10^{18} and less than $1.2 \times 10^{16} cm^{-3}$ respectively. The 6-inch diameter wafer was divided into five parts and each part was subjected to the following treatments:

  A control, as grown
  B specimen A annealed 1000 °C, 24h
  C specimens A with high-low-medium gettering anneal (1000 °C, 24h)-(700 °C, 24h)-(850 °C, 24h)
  D specimen A with Ni diffusion 1000 °C, 24h
  E specimens D with high-low-medium gettering anneal (1000 °C, 24h) - (700 °C, 24h)-(850 °C, 24h)

Before the above treatments, each slice was subjected to a standard cleaning procedure similar to that of Wu and Witty (1978). For diffusion, 99.995% pure Ni was evaporated under a vacuum pressure of about 10^{-4} Pa onto the unpolished back surface of diffused specimens. Diffusion and gettering anneal were carried out in a tube furnace under an oxygen atmosphere. Specimens were gradually quenched to room temperature after each thermal treatment by moving them to one end of the furnace tube. After diffusion, the remaining Ni film was etched off the back surface before gettering anneal commenced. Resistivity measurements were performed by means of a computer controlled four-point probe system which also calculates the carrier concentration values. Lifetime measurements were performed by the photoelectromagnetic-photoconductive PEM-PC method (Pissari and Susi, 1983; Carotta et al., 1986). Interstitial oxygen and substitutional carbon content measurements were carried out by means of a computer controlled Bruker Fourier Transform Infra-Red (FTIR) spectrometer.

3. Results and Discussion

The results obtained from the resistivity, lifetime and infrared absorption spectroscopy measurements together with relevant diffusion data are shown in Table 1. Also shown in Table 1 is the computed donor density value, N_d, values were derived from comparison of the acceptor densities of the Ni-diffused and control specimens following resistivity measurements. The O_i contents on Table 1 were obtained by using the ASTM (American Society for Testing Materials) standard calibration of $2.5 \times 10^{17} cm^{-3}$. The post anneal C_s content of the substrate still remained less than $10^{16} cm^{-3}$.

Comparison of specimens A and B of Table 1 shows that annealing of specimen B at 1000°C for 24h resulted in about 7% reduction in the O_i content, about 20% reduction in the minority carrier lifetime and little or no change in resistivity value. The relative stability in the resistivity value of specimen B after annealing is an indication that contamination by shallow impurities from the annealing system, if any, is negligible. In addition, no new donors (ND) or thermal donors (TD) are expected to be generated at an annealing temperature of 1000°C (Cazcarra and Zunino, 1980; Kanamori and Kanamori, 1979). Hence no significant change in the resistivity value is expected, as observed. However, the reduction of about 20% in lifetime value of specimen B with respect to specimen A can be attributed to some low density of oxygen related deep levels defects, which may be formed after a single-step high temperature annealing, as observed by Bender (1984) and Schmalz et al (1987). In other words, apart from the expected outdiffusion of some of O_i content, some oxygen related deep level defects could in addition lead to the observed 7% reduction in the O_i content of specimen B with respect to specimen A. For specimen C, Table 1 shows that after the three-step thermal cycle, the resistivity value is still relatively stable but there is evidence of O_i outdiffusion and or oxygen precipitation as the final O_i concentration is about 80% of the initial value. In addition, there is about 38% reduction in the lifetime value with respect to specimen A. It is known that generation of oxygen precipitates in the bulk of Cz substrates, following a heat treatment, leads to the formation of deep-level defects which reduce the minority carrier recombination lifetime significantly (Hwang and Scvhoroeder, 1986). The reduction of the lifetime value from 28.4 μs to 17.6 μs in specimen C can, therefore, be attributed to the presence of oxygen precipitates in the substrate.

For analysis, we shall assume the solubility value ($3.5 \times 10^{17} cm^{-3}$) of Ni at the diffusing temperature of 1000 °C (Weber, 1983) as the concentration of nickel atoms in our Ni-diffused specimens. This assumption can be justified under our experimental condition since Ni is known to be a fast diffusant in Si (Weber, 1983). Comparing specimens B and D, Table 1 shows that the addition of Ni impurity to the silicon substrate resulted in a minor increase in the resistivity value, a significant reduction in the minority carrier lifetime value from 22.7 μs to 5.3 μs in specimen D and a considerable reduction in the O_i content from $2.5 \times 10^{17} cm^{-3}$ in specimen B to $0.88 \times 10^{18} cm^{-3}$ in specimen D. There is still a divergence of opinions

Table 1: Relevant diffusion data, resistivity, lifetime and oxygen precipitation measurement results in Ni diffused p-type Cz silicon

Specimen	A	B	C	D	E
Ni diffusion temp (°C) Under O_2 for 24h	-	-	-	1000	1000
N_{Ni} (10^{17}cm^{-3}) from solubility data [1]	-	-	-	3.5	3.5
Temperature (°C) and time (h) of anneal under O_2	-	1000,24	1000,24 700,24 850,24	-	1000,24 700,24 850,24
Resistivity (ohm-cm) ±2%	5.40	5.42	5.43	5.57	5.50
Acceptor density N_a(10^{15}cm^{-3})	2.49	2.49	2.48	2.42	2.45
Donor density N_d (10^{13}cm^{-3}) due to N_{Ni}	-	-	-	7.0	4.0
Minority carrier lifetime T_n(10^6s)) ±2%	28.40	22.70	17.60	5.30	12.80
Interstitial oxygen density O_i(10^{18}cm^{-3}) ±2%	1.10	1.02	0.88	0.97	0.56
Out-diffused/precipitated oxygen ΔO_i (10^{17}cm^{-3})	-	0.80	2.20	1.40	5.40

on the electrical activity of Ni in silicon. While some researchers report Ni as only an acceptor (Milnes, 1973; Pearton and Tavendale, 1983), some report it as only a donor (Graff and Pieper, 1981) and others (Lemke, 1987; Kitagawa and Nakashima, 1989; Kitagawa et al., 1991) indicate it is amphoteric. The donor level has been reported to be around 0.17 eV from the valence band. In addition, Yoshida and Saito (1967) have reported that only about one in every thousand diffusing Ni atoms remains in the electrically active site. Despite the above controversy, the donor nature of nickel in our p-type substrate is clearly shown in Table 1 as the introduction on Ni into specimen D led to a partial compensation of the acceptor density, thus resulting in a low level of donor concentration. This low level of donor activity (7×10^{13}cm^{-3}) resulting from a nickel atom concentration of about 3.5×10^{17}cm^{-3} agrees well with the reports of Yoshida and Saito (1967) and Kitagawa et al (1991) and the fact that Ni has a donor energy level of E+0.17 eV in silicon. With an activation energy of 0.17 eV one would expect only about 10% ionization of this donor level at room temperature. Majority of the diffused Ni impurity may exist in the form of precipitates in the bulk of the substrate as observed by Shen et al. (1996) since our specimen was cooled rapidly. When compared with specimen B, specimen D shows that the addition of the nickel impurity resulted in about 77% reduction in the minority carrier lifetime. This reduction is a manifestation of the presence of deep-level traps or recombination centers due to the incorporation of Ni into specimen D. Table 1 also shows a reduction of about 5% in the O_i content of specimen D with respect to specimen B. This reduction which has also been noted by Pearton and Tavendale (1983) is an indication of a possible

reaction of the Ni impurity with O_i and may be exploited in the gettering of Ni impurity in the Cz silicon.

The gettering effect of the oxygen precipitates on the contaminating Ni impurity is reflected in the minority carrier lifetime values of specimens B, D and E of Table 1. While the introduction of Ni impurity reduced the lifetime from 22.7 µs in specimen B to 5.3 µs in specimen D, the presence of gettering oxygen precipitates increased it from 5.3 µs to 12.8 µs in specimen E. The reduction in lifetime in specimen D is an indication of the introduction of deep levels while the increase in specimen E reflects the reduction in the density of the deep levels. The magnitude of the relative density of the deep levels introduced into the specimens as a result of annealing and impurity diffusion can be obtained from the expression (Adegboyega and Poggi, 1994),

$$N_t = c\tau^{-1} \qquad (1)$$

where N_t is the trap density resulting from the presence of deep level impurities and recombination centers, c is a constant and $\ddot{A}$ is the experimental value of minority carrier lifetimes measured at a particular temperature. If the lifetime values for specimens B to E from Table 1 are substituted into (1), we would obtain:

$$N_{tB} = 0.04c, N_{tC} = 0.06c, N_{tD} = 0.20c, N_{tE} = 0.08c \qquad (2)$$

Comparison of the N_{tC} and N_{tD} values of (2) shows that the density of the deep-level traps arising from oxygen precipitates in specimen C is about 30% of that due to the incorporation of Ni impurity atoms into specimen D. Also, a comparison of values N_{tD} and N_{tE} values shows that the presence of the gettering oxygen precipitates in specimen E led to

about 60% reduction in the Ni related deep-level trap density of specimen D. A higher degree of gettering efficiency would result if a lightly contaminated specimen, especially at contamination levels found in unintentionally contaminated substrates, is considered. It is interesting to note that the reduction in the Ni related deep-level trap density of specimen E with respect to specimen D due to the gettering effect is also accompanied by a corresponding reduction in nickel donor concentration. This confirms that the donor effect observed in the specimens is indeed due to nickel impurities.

4. Conclusion

Nickel showed a donor type activity in p-type Cz silicon but less than one in every thousand atoms present remains in the electrically active state. Apart from generating deep-level traps, there is evidence that the presence of Ni impurity led to a reduction in the concentration of the interstitial oxygen content of contaminated specimens. High temperature oxygen precipitates act as efficient gettering sink for the nickel impurity.

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