Room Temperature Photoluminescence Characterization of Low Dose As⁺ Implanted Si after Rapid Thermal Annealing

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Arsenic (As⁺ 150 keV, 1.0 × 10¹³ cm⁻²) implanted p−Si(100) wafers were spike annealed at 1100°C for 1 s in a commercially available rapid thermal annealing (RTA) system. Significant variations in sheet resistance were observed while As dopant profiles, measured by secondary ion mass spectroscopy (SIMS), were almost identical. Photoluminescence (PL) spectra were measured from all wafers under three different excitation wavelengths (532, 650 and 827 nm) at room temperature. PL spectra showed large intensity variation, corresponding to the sheet resistance. PL excitation wavelength dependence suggests the variation in density of residual damage as the possible cause of sheet resistance variation.

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Charge coupled devices (CCDs) have been widely used in scientific instruments and digital cameras until recently.1 The gate structure used in CCDs to transfer electrical charges (image data) to the edge of the sensor, requires a separate power source (more power) and sequential data transfer (slower speed).2,3

For portable device applications, smaller devices with low power consumption are strongly desired. Complementary metal-oxide-semiconductor (CMOS) image sensors, with reduced power consumption and fast data transfer, have become a common alternative choice for image sensors.5 These devices consist of large arrays of photodiodes and amplifiers. The photodiodes accumulate electrical charge and increase voltage when exposed to light. The voltage is amplified and transmitted as electrical signals. Since the CMOS image sensors have the same basic structure as CMOS memory devices, they are cost effectively mass produced, using well-established manufacturing technology.1

Generally, CMOS image sensors generate more electrical noise than CCDs and can result in poor image quality due to performance fluctuations in the large array of photodiodes and amplifiers.3 Small performance differences in photodiodes and amplifiers can result in noise in the output image. The noise problem increases as cell size is reduced and the number of cells in a chip increases. Noise reduction approaches commonly used to overcome this problem are; improved device level performance variation and reduction of the variation of background noise. Device-level noise reduction efforts are also becoming increasingly important.5

High energy, low dose ion implant conditions are often used in CMOS image sensor fabrication processes. Average dopant concentration in the implanted junctions are 2 ~ 3 orders of magnitude lower than those of advanced CMOS logic and memory devices. Small amounts of defects and residual damage have a significant impact in the electrical properties of implanted junctions after RTA. To reduce noise in CMOS image sensors, elimination of defects and residual damage are very important steps. The room temperature photoluminescence (RTPL) technique can be used for finding and reducing the electrically active and/or non-radiative defects and damage in the early stage of CMOS image sensor fabrication steps.

It is well known that metal contamination, poor surface passivation, residual implant damage, and defects contribute to dark current noise (fixed-pattern noise) generation.5,6 To prevent undesired problems, metal contamination levels and process fluctuations during manufacturing are constantly monitored using monitor wafers. Implant anneal processes have historically been monitored by sheet resistance measurement using a four point probe, for dopant activation characterization, and secondary ion mass spectroscopy (SIMS), for dopant depth profiling.7,8 However, conventional characterization techniques often overlook problems due to their insensitivity to surface passivation quality, residual implant damage and defects.

Deep level transient spectroscopy (DLTS) and positron annihilation spectroscopy (PAS) have been applied to characterize the low density residual defects which influence electronic properties of implanted Si after dopant activation annealing.9–11 Recently, detailed thermal behavior of residual damage in low-dose arsenic (As) and boron (B) implanted Si, after high-temperature rapid thermal annealing (RTA), has been investigated using cathode luminescence (CL).12–14 However, most of these characterization techniques require sample preparation and restrict sample size. A non-destructive (hopefully non-contact, as well) characterization technique, without special sample preparation and sample size limitation, is desired for in-line monitoring of potential process and/or equipment related problems.

Interband photoluminescence (PL) of crystalline Si, at room temperature and wavelengths near 1.1 μm, is very sensitive to the density of non-radiative bulk and surface defects.15,16 It makes measurement of defect concentration, using RTPL, possible. Monitoring of surface defect formation during oxidation processes, after wet etching, and epitaxial Si minor carrier diffusion length, by RTPL, has been reported previously.17,18 Promising results of RT spectroscopic PL studies on ultra-shallow and shallow implanted junctions have also been reported previously.19–22 RTPL characterization of non-radiative defect density on surfaces and interfaces of Si with native, anodic and thin thermal oxides, have been extensively studied under ultra violet (UV) excitation in vacuum by Timoshenko et al.23

In this paper, RTPL was investigated using implant annealed Si samples, which showed electrical performance variations, even though all the (implant and anneal) process conditions are substantially the same. The major objectives are to understand the main cause of electrical performance variations and develop a practical implant monitoring technique for CMOS image sensor process control.

Low dose, arsenic implanted (As⁺ 150 keV 1.0 × 10¹³ cm⁻²) p−Si(100) wafers, used in CMOS image sensor processing, were prepared. The As⁺ implantation was done through 15.7 nm thick thermally grown SiO₂ films on p−Si(100) wafers. The wafer diameter used in this study is 200 mm. The wafers were spike annealed at 1100°C for 1 s in a commercially available RTA system. The RTA was done in the presence of a small amount of O₂ (~100 ppm) in 1 atm N₂. The low dose, As⁺ implanted Si wafers, annealed at high temperature for a very short time (~1 s or less), often results in a large variation in electrical activation. Thus, sheet resistance of annealed wafers is regularly measured to monitor the RTA tool performance and control the RTA process within quality control limits. The chamber-to-chamber device performance variations often become an issue in device manufacturing fabs.
To identify the root cause of sheet resistance variations in the low dose As$^+$ implanted wafers, after spike RTA at 1100°C for 1 s, one as-implanted wafer and eight spike annealed wafers, with significant sheet resistance variations, were selected for RTPL study. RTPL spectra were measured from all wafers, in air, under three excitation wavelengths (532, 650 and 827 nm) with different penetration depths (1.5 ~ 10 μm from the surface). A specially designed spectrograph with a thermoelectrically cooled InGaAs linear diode array (Wafer-Masters MPL-300) was used for RTPL measurements. Beam size on the wafer was approximately 50 μm in diameter. The excitation laser power at the wafer surface was in the range of 20 ~ 50 mW. The RTPL spectra were measured in the wavelength range of 950 ~ 1350 nm. Sheet resistance and As depth profiles of the as-implanted wafers, and eight annealed wafers, were measured by a four point probe and SIMS.

Figure 1 shows the sheet resistance values of the as-implanted wafer and eight spike annealed wafers. Despite all the wafers being heat treated under the same, nominal, spike annealing condition of 1100°C for 1 s, the sheet resistance values fell into three groups: >10 kΩ/sq., ~1.6 kΩ/sq and ~1.5 kΩ/sq. The sheet resistance of the as-implanted wafer was measured to be ~40 kΩ/sq. It is empirically known that the sheet resistance values ~1.5 kΩ/sq., after spike RTA, results in higher device yield. The sheet resistance value ~1.6 kΩ/sq, results in poor device yield. The wafers with sheet resistance values >2.0 kΩ/sq. are not suitable for device fabrication. Thus, the target sheet resistance value, after spike RTA, was set at ~1.5 kΩ/sq. The sheet resistance variations within wafer were typically less than 1% of average sheet resistance. The wafer-to-wafer sheet resistance variations, under the same RTA conditions and in the same RTA systems, are less than 5% of average sheet resistance values. To understand the root cause of sheet resistance variations, under the same nominal spike RTA condition, the system data logs are routinely verified, but are not conclusive. There are insufficient data points available for comparison, because of the short annealing time. The high temperature spike annealing aspect of this study lead us to suspect possible redistribution or diffusion of As atoms during spike RTA.

To investigate the possible cause of the large variation of sheet resistance values (1.5 ~ 45 kΩ/sq.) of the annealed wafers, Arsenic depth profiling was done by SIMS. Figure 2 shows the Arsenic depth profiles of the as-implanted wafer and eight spike annealed wafers. The maximum As concentration of 8.6 × 10$^{17}$ cm$^{-3}$ was measured at ~90 nm from the surface. The As depth profiles of all nine wafers (as-implanted and eight annealed wafers) were superimposed on top of each other. No As diffusion was observed within the resolution of SIMS. Background boron (B) concentrations of the p$^-$Si wafers were also measured by SIMS. The background B concentration was constant at ~1.8 × 10$^{15}$ cm$^{-3}$ for all wafers. No abnormality was found from SIMS analysis. Since the annealing time is very short and the solid solubility of As in Si at 1100°C, is ~3.6 × 10$^{20}$ cm$^{-3}$ (~2.5 orders of magnitude higher than the maximum As concentration of 8.6 × 10$^{17}$ cm$^{-3}$), the solid solubility of As in Si at 700°C (8.0 × 10$^{19}$ cm$^{-3}$) is still two orders of magnitude higher than the maximum As concentration. Thus, As diffusion during spike RTA can be neglected, as verified by SIMS depth profiles.

Multiwavelength RTPL measurements were done for all wafers. The wide range of sheet resistance values of 1.5 ~ 45 kΩ/sq., under the same RTA conditions, can only be explained by variations in dopant activation, passivation quality, interface quality and residual crystalline damage, since the possibility of As diffusion during spike RTA was eliminated. RTPL measurements should be able to reveal the possible causes of the large variation of sheet resistance values (1.5 ~ 45 kΩ/sq.) despite almost identical As depth profiles, since the efficiency of the interband RTPL is limited by the density and location of non-radiative bulk and surface defects. Multiwavelength RTPL, with a range of penetration depths, can provide virtual depth profiling results on non-radiative defects and recombination centers. Penetration depths of the three excitation wavelengths (532, 650 and 827 nm), relative to the junction depth of 0.65 μm (As concentration of 1.8 × 10$^{15}$ cm$^{-3}$ assuming 100% dopant activation), were illustrated as a part of Fig. 2.

Figure 3a ~ 3c show RTPL spectra of all wafers in the wavelength range of 950 ~ 1350 nm under, 532, 650 and 827 nm excitation. For easy comparison, the scale of vertical (RTPL intensity) axes was kept the same. Arsenic implanted wafers before RTA showed almost no RTPL signal, regardless of excitation wavelength (or penetration depth). A very weak RTPL peak, at ~1140 nm, was barely recognizable from the as-implanted wafer under 827 nm excitation, with penetration depth of ~10.0 μm (~15 times deeper than the junction depth of ~0.65 μm). All wafers showed weak RTPL signals after RTA under 532 nm excitation. The as-implanted wafer and wafers A ~ F, with the sheet resistance range of 1.6 ~ 45 kΩ/sq., showed significantly weaker RTPL signals compared to the annealed wafers G ~ I with sheet resistance ~1.5 kΩ/sq., under 650 and 827 nm excitation, with deeper penetration depths.

The interband RTPL of crystalline Si near 1.1 μm is very sensitive to the density of non-radiative bulk and surface defects.15,16

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**Figure 1.** Sheet resistance of As$^+$ implanted (150 keV 1.0 × 10$^{13}$ cm$^{-2}$) p$^-$Si (100) wafers before and after RTA at 1100°C for 1 s.

**Figure 2.** SIMS depth profiles of nine As$^+$ implanted (150 keV 1.0 × 10$^{13}$ cm$^{-2}$) p$^-$Si (100) wafers before and after RTA at 1100°C for 1 s. Probing depths of PL under different excitation wavelengths are shown for comparison.
Interband RTPL has also been used in monitoring surface and interface defects during oxidation, epitaxial Si quality and electrical activation of low energy implanted Si after RTA.\textsuperscript{15-23} The effective lifetime in semiconductors is important to the operation of some semiconductor devices such as solar cells, pn junctions, bipolar junction transistors and thyristors, but it is generally difficult to decompose into bulk recombination lifetime and surface recombination velocity.\textsuperscript{25,26} Correlation lifetime and PL intensity near 1.1 μm has been studied in bulk Si and SOI (silicon-on-insulator) wafers under various excitation wavelengths.\textsuperscript{26,27} RTPL near 1.1 μm and electron beam-induced current (EBIC) recombination behavior of crystal defects in multicrystalline silicon were also studied for solar cell applications.\textsuperscript{28} The interband RTPL of Si near 1.1 μm can provide very useful insights on crystallinity and electrical properties which affect CMOS image sensor performance.

Based on the excitation wavelength dependence of RTPL spectra, the wafers annealed in the chamber have considerable defects and residual damage, at, or below, the implanted layer. Wafers B, C and D, with sheet resistance >10 kΩ/sq., showed weak PL signals under all three excitation wavelengths. Wafers E and F, with the sheet resistance values of ~1.6 kΩ/sq., showed even weaker PL signals than wafers B, C and D. They seemed to have considerable defects and residual damage to be repaired by the RTA step. It is somewhat surprising to see the decrease of PL signals with decreasing sheet resistance (or increase of dopant activation). The As motion, by vacancy and interstitially,\textsuperscript{29} during dopant activating RTA, can be suspected. Wafers G, H and I showed sheet resistance values ~1.5 kΩ/sq. (~0.1 kΩ/sq. smaller than that of wafers E and F). The ~6.2% reduction of sheet resistance from wafers E and F was observed in RTPL intensity (under 650 and 827 nm excitation) as a 3 ~ 4 fold (300 ~ 400%) increase.

RTPL measurement is not only a non-contact characterization technique, but is also 50 ~ 60 times more sensitive than sheet resistance measurements in detecting the presence of defects and residual damage, which may result in compromised electrical performance. This strongly suggests that there is a threshold defect and residual damage concentration for acceptable sheet resistance values (electrical activation and eventually device performance). Figure 4 shows the PL intensity (a) and PL intensity ratio (b) of as-implanted and annealed wafers, under three different excitation wavelengths. Among the spike RTA wafers G, H and I, the comparison of RTPL intensity from 650 nm excited RTPL to that of 827 nm excited RTPL shows significant differences. The spike annealed wafer, I, showed strong PL signals under 650 and 827 nm excitation. It suggests that the density of defects and residual damage in this wafer is lower than in wafers G and H, even though the sheet resistance values are almost identical (~1.5 kΩ/sq.).

The intensity ratio of 650 nm excited PL signal to the 827 nm excited PL signal can be used as a strong indicator for the degree of defect densities and residual damage in implant annealed Si. Wafers with a strong 650 nm PL intensity and a PL intensity ratio (I\textsubscript{650nm}/I\textsubscript{827nm}) have the highest crystal quality (or have the lowest density of defects and damages).

Both 650 and 827 nm excited RTPL intensities of wafers G, H and I are stronger than for the rest of the wafers, as seen in Fig. 4b. This can be interpreted as evidence of reduced trap density in the order of probing depths of 650 and 827 nm (i.e. ~4.0 and ~10.0 μm). Wafer G only showed RTPL intensity increase under 650 and 827 nm excitation over wafers A ~ F. Wafers H and I showed RTPL intensity
increase under all three excitation wavelengths. Wafer H resulted in the highest RTP intensity and second highest RTP intensity under 650 and 827 nm excitations, respectively. The second highest RTP intensity, wafer H under 827 nm excitation, suggests that there are non-negligible amounts of traps beyond the probing depth of 650 nm excitation. Among the three wafers, wafer I, with the strong RTP intensity under all excitation wavelengths, seemed to have the highest crystal quality after implant annealing because it gives highest RTP signal under all excitation wavelengths. The RTP intensity under various excitation wavelengths is a good indication of the trap density of generated electron-hole pairs, approximately on the order of corresponding probing depths. Higher RTP intensity under a given excitation wavelength can be interpreted as higher crystal quality (or lower trap density). RTP intensity under various excitation wavelengths, and its ratios, can be used as a valuable crystal quality indicator at various depths.

Based on the sheet resistance measurement and SIMS depth profiling results, the major cause of the sheet resistance and RTP intensity variation among spike annealed wafers is due to poor process control, including the lack of RTA system process repeatability. In fact, significant efforts have been made to match process performance among RTA systems. Since the system control algorithms rely on inputs from various sensors, combinations of sensor mis-calibrations can produce unexpected results. Frequent monitoring and calibration of process results and equipment conditions, using sufficiently sensitive and reliable monitoring techniques, are required for establishment of robust process. The RTP charaterization technique can provide an additional dimension of understanding the physics of the implant annealing process toward process optimization and control.

Recent CL studies of low-dose As⁺ and B⁺ implanted Si after dopant activation anneal revealed that the specifics of annealing techniques and temperature control are very important to reduce undesirable residual damage after high temperature (>1100 °C) dopant activation RTA.12–14 The defects remaining after RTA were characterized to be vacancy-type defects created during extremely rapid (non-equilibrium) cooling steps of the RTA sequence. Additional thermal equilibrium (or isothermal) heating in a furnace-type system, even at 300–400 °C, gradually reduces the residual defects. However, carbon- and oxygen-related point defects were newly created in the range of 500–600 °C. These defects are generally eliminated at 700 °C. This indicates an additional equilibrium thermal treatment at >700 °C is advisable to remove residual damage, as well as to activate impurities after the conventional non-equilibrium RTA at high temperature.

Due to the nature of RTA processes, exact thermal cycling history and matching of every point, within wafer and wafer-to-wafer, is almost impossible. The RTA process tends to add more variations in material properties. Most of the time, the main positive effect outweighs the negative side effect so that we cannot recognize the existence of the side effects. However, the side effects of non-equilibrium RTA process steps cannot be ignored in electronic noise sensitive applications such as image sensors.

High densities of non-radiative recombination centers, such as defects and residual damages, increases the total capture cross section for generated electron-hole pairs. As a result, the lifetime of carriers (electrons and holes) are significantly shortened and RTP intensity is rapidly diminished. CMOS image sensor cells fabricated from wafer areas showing shorter carrier lifetime would naturally lose charge (image signal) and thus, a device from such an area would show deteriorated performance, even if the device is not completely compromised. To tightly control device performance variations within a chip (a large array of photodiodes and amplifiers), within wafer and wafer-to-wafer, in-line monitoring of carrier behaviors using multi-wavelength photoluminescence can be extremely beneficial.

Multiwavelength RTP intensity characterizes the approximate depth distribution of non-radiative recombination centers (such as defects and residual damages) and provides valuable insights into projected electrical properties and performance of implanted junctions augmenting the usefulness of conventional sheet resistance measurements (using a four point probe) and SIMS analysis. In addition to the non-contact, nondestructive nature of PL, multiwavelength excitation can provide virtual depth profiling of defects and residual damage in implanted wafers after dopant activation annealing. It can also be used for non-contact in-line monitoring of passivation, dielectrics/semiconductor interface and junction integrity.

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