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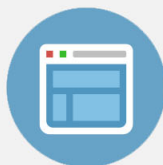
# Outdiffusion of Be during rapid thermal annealing of high-dose Be-implanted GaAs

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The outdiffusion of Be implanted into GaAs has been found to be identical after capless or capped ($Si_3N_4$ or $SiO_2$) rapid thermal annealing (RTA) at 900–1000 °C and to depend on the Be dose and its proximity to the surface. The outdiffusion is more pronounced when the Be implant is shallow ($< 0.1$ $\mu$m) and/or the $Be^+$ dose is high ($> 1 \times 10^{15}$ $cm^{-2}$). It is demonstrated that the Be outdiffusion is driven by the presence of a highly damaged surface layer. Auger results suggest the formation of a $BeO_x$ compound at the surface of a high-dose ($1 \times 10^{16}$ $cm^{-2}$) Be-implanted sample that underwent capless RTA at 1000 °C/1 s. It appears that $BeO_x$ formation occurs when the outdiffused Be interacts with the native Ga/As oxides during annealing. All the Be remaining in the GaAs after a $> 900$ °C/2 s RTA is electrically active.

Beryllium implanted into GaAs at high doses ($> 1 \times 10^{13}$ $cm^{-2}$) is known to outdiffuse during subsequent furnace annealing at $> 700$ °C.[1-5] The use of rapid thermal annealing (RTA) in an Ar or arsine ambient reduces this outdiffusion only marginally, even for significantly shorter annealing times.[6] Co-implantation of N, F, P, or As ions together with Be has been reported to reduce the Be outdiffusion and to improve electrical activation.[7] In the present study, Be outdiffusion was investigated in capless as well as capped GaAs during RTA as a function of $Be^+$ dose and energy. The results suggest that a highly damaged layer exists at the surface of high-dose implanted GaAs into which Be segregates during annealing. This Be also appears to interact with the native oxide at the GaAs surface.

Semi-insulating $\langle 100 \rangle$ GaAs wafers were implanted with $Be^+$ in the dose range $1 \times 10^{12}$–$1 \times 10^{16}$ $cm^{-2}$ at energies from 10 to 100 keV. For capped studies, a 500-Å $Si_3N_4$ film was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 300 °C. Capping with $SiO_2$ was also used on a limited number of samples. The samples were annealed in a purified Ar ambient in the temperature range of 700–1000 °C for durations of 1–300 s. Sheet resistivity and Hall measurements, and secondary ion mass spectroscopy (SIMS) were performed to study the outdiffusion. Cross-sectional transmission electron microscopy (XTEM) was also performed on Be alone and Be/Ar co-implanted samples to study Be gettering to damage.

Table I summarizes the amount of Be retained in the GaAs as measured by SIMS under a variety of $Be^+$ dose/energy conditions. All the implanted samples underwent capped RTA at 900 °C in Ar ambient. Identical outdiffusion results were obtained when the samples were annealed in arsine ambient with or without a cap. In all cases, no outdiffusion occurred when the Be peak concentration was $< 2 \times 10^{18}$ $cm^{-3}$ (e.g., in 10-keV $1 \times 10^{12}$ $cm^{-2}$ or 60-keV

$1 \times 10^{13}$ $cm^{-2}$ implanted samples). However, when the $Be^+$ peak concentration exceeded $1 \times 10^{19}$ $cm^{-3}$ in the high-dose implanted ($> 1 \times 10^{15}$ $cm^{-2}$) samples, Be diffused rapidly toward the GaAs surface. Figure 1 shows pronounced outdiffusion in the samples implanted at 10 or 60 keV at a dose of $1 \times 10^{15}$ $cm^{-2}$ and subsequently annealed at 900 °C for 2 s. In the samples implanted at 10 keV only 3% of the implanted Be remained in the substrate after the annealing. However, in the 60-keV implanted samples, the fraction of Be remaining was 80%. The outdiffusion continued as the annealing proceeded and the Be fraction decreased to 40 and 15%, respectively, for 30- and 300-s anneals. Figure 2 shows the out diffused fraction of the implanted Be measured by SIMS after a 900 °C/2 s RTA as a function of the Be dose for energies of 10, 60, and 100 keV. The outdiffusion is most pronounced for low-energy/high-dose Be implants.

Since the SIMS profiles as well as electrical results from capless or $Si_3N_4$ capped samples are identical, the role of $Si_3N_4$/GaAs interfacial stress on Be outdiffusion cannot be significant. This is further supported by an experiment where a limited number of anneals were done with an $SiO_2$

TABLE I. Implanted vs remaining Be dose in the capped GaAs samples after RTA at 900 °C for 30 and 300 s. The SIMS and electrical activation data were equivalent for the annealed samples as 100% of the remaining Be activated during the annealing.

| Implant energy (keV) | Implant dose ($cm^{-2}$) | Remaining Be dose ($cm^{-2}$) | |
|---|---|---|---|
| | | 30 s | 300 s |
| | | ... | ... |
| 10 | $1.0 \times 10^{13}$ | $2.5 \times 10^{12}$ | $1.0 \times 10^{12}$ |
| | $1.0 \times 10^{14}$ | $4.5 \times 10^{12}$ | $2.5 \times 10^{12}$ |
| | $1.0 \times 10^{15}$ | $2.0 \times 10^{13}$ | $1.0 \times 10^{13}$ |
| 20 | $1.0 \times 10^{15}$ | $6.5 \times 10^{13}$ | $3.0 \times 10^{13}$ |
| 60 | $1.0 \times 10^{13}$ | $1.0 \times 10^{13}$ | $1.0 \times 10^{13}$ |
| | $1.0 \times 10^{14}$ | $9.0 \times 10^{13}$ | $7.0 \times 10^{13}$ |
| | $1.0 \times 10^{16}$ | $4.0 \times 10^{14}$ | $1.5 \times 10^{14}$ |
| 100 | $1.0 \times 10^{15}$ | $8.0 \times 10^{14}$ | $6.0 \times 10^{14}$ |

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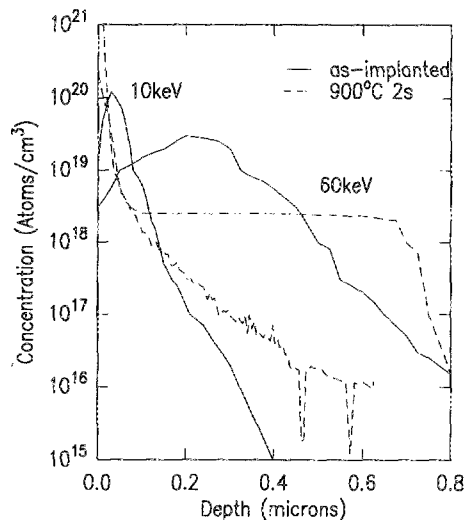
FIG. 1. SIMS analysis of 10-keV, $1 \times 10^{15}$ cm$^{-2}$ and 60-keV, $1 \times 10^{15}$ cm$^{-2}$ Be$^+$ implants into GaAs, before and after annealing at 900 °C/2 s in Ar. The Be segregates preferentially towards the surface of the GaAs.



FIG. 3. Segregation of Be to the Ar implantation induced damage region during capless RTA at 900 °C for 2 s. (a) An XTEM micrograph showing the damage distribution in the Be (20 keV, $1 \times 10^{15}$ cm$^{-2}$) + Ar (60 keV $1 \times 10^{14}$ cm$^{-2}$) co-implanted sample. (b) The SIMS distributions of Be alone before and after the annealing as well as Be + Ar after the annealing.

cap and again identical electrical results were obtained. These results strongly indicate the driving force for the Be outdiffusion must exist within the implanted substrate. Since Be is known to diffuse interstitially and its diffusion coefficient is enhanced in the presence of damage,[4] a possible cause of outdiffusion may be Be segregation to a highly damaged surface layer produced by the high-dose Be implant itself.

In order to confirm that the presence of a heavily damage region at the surface can indeed cause Be segregation to the surface, an experiment was conducted in which Ar was co-implanted at 60 keV ($1 \times 10^{14}$ cm$^{-2}$) into a Be-implanted sample (20 keV, $1 \times 10^{15}$ cm$^{-2}$). Under these implant conditions, the peak of the Ar distribution ($\sim$450 Å) was shallower than that of the Be ($\sim$750 Å). The XTEM (Fig. 3) revealed damage clusters in the region (0–550 Å) where Ar was implanted. The XTEM micrograph and the SIMS profiles of Be before and after RTA at 900 °C/2 s are compared
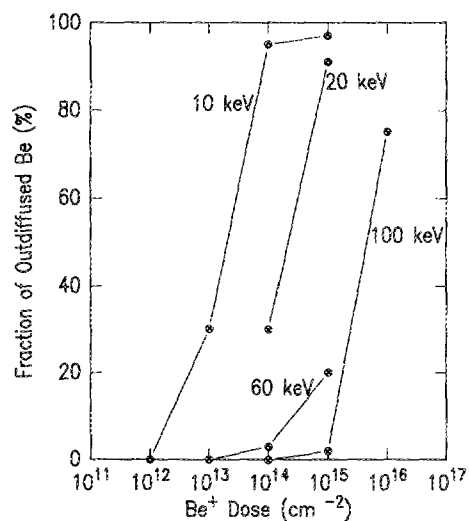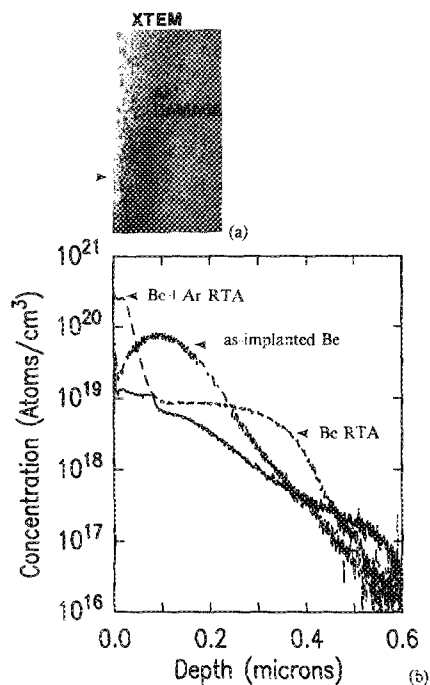
in Fig. 3. It is clear that pronounced Be segregation occurs to the argon-induced damage region during the annealing. The Be redistribution in this sample is reminiscent of that observed in Fig. 1. To further substantiate the role of surface damage on Be outdiffusion, 500 Å was removed chemically ($H_3PO_4$:$H_2O_2$: $H_2O$, 3:1:50 at 0 °C) from a 100-keV, $1 \times 10^{15}$ cm$^{-2}$ implanted GaAs sample prior to annealing. The SIMS profile from this sample after RTA at 900 °C/2 s shows that although significant redistribution of the Be still occurs, Be no longer outdiffuses. It is remarkable that nearly 100% Be remained within the substrate after the annealing.

In order to better understand the chemical nature of the Be accumulated at the surface during annealing, a GaAs sample implanted with the highest dose of Be ($1 \times 10^{16}$ cm$^{-2}$) and subsequently annealed at a relatively high temperature (1000 °C/1 s) was analyzed by scanning Auger electron spectroscopy (AES). A strong Be (30 at. %) peak at the surface was observed in the Auger spectrum in agreement with the SIMS data. However, the position of Be peak (95 eV) in the spectrum was shifted by 9-eV with respect to the pure Be peak position (at 104 eV) and corresponded to that of Be in BeO.[8] Furthermore, the Auger data as a function of depth show that Be and O track each other in the near-surface region ($< 100$ Å) (Fig. 4). Both of these results implied that a BeO$_x$ compound is present in the surface region of the GaAs. High-dose Be implantation can indeed cause atomic displacements/recoils from the surface native oxide, leading to the formation of a stable BeO$_x$. Also, due to the presence of native Ga/As oxides ($Ga_2O$, $Ga_2O_3$, $As_2O_3$), the segregated Be can be chemically bounded up at the surface by the oxides. Based on reaction free energies of



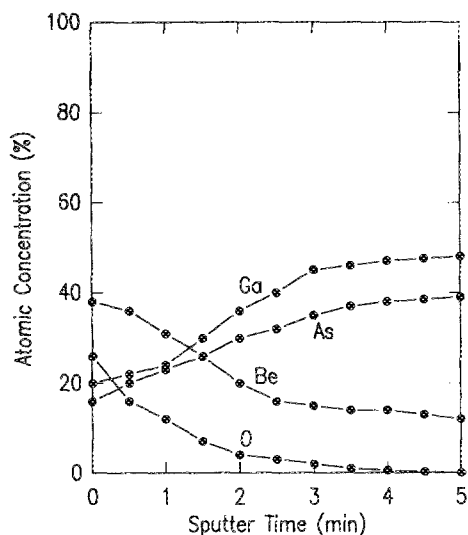FIG. 2. Fraction of the implanted Be outdiffused during capless RTA at 900 °C/2 s under a variety of implant conditions.

FIG. 4. Auger depth profiles of Ga, As, Be, and O from the sample implanted with Be at 100 keV to a dose of $1 \times 10^{16}$ cm$^{-2}$ and subsequently capless annealed at 1000 °C/1 s in Ar ambient. Note that the Be and O track each other in the near-surface region.

Be/O, Ga/O, and As/O, Be should be able to reduce $Ga_2O$ and $As_2O_3$ during the annealing. The total depth of the

BeO$_x$ is $<100$ Å, which would require approximately $6 \times 10^{15}$ cm$^{-2}$ of Be. The Hall data from this sample showed 75% loss in electrical activation which agrees reasonably well with the Auger data. At lower Be doses (e.g., Be, 100 keV, $1 \times 10^{15}$ cm$^{-2}$), it was difficult to detect Be unambiguously by Auger analysis because of a weak Be signal from such samples.

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# KrF/H₂ Raman conversion at high repetition rate using a hydrogen gas circulating system

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A decrease of Raman conversion efficiency pumped by KrF excimer laser at high repetition rate was observed in a sealed hydrogen Raman cell. A hydrogen gas circulating system was designed with gas pressure up to 50 atm; it can be operated at a high repetition rate without decrease of Raman conversion efficiency.

Stimulated Raman scattering of ultraviolet excimer laser radiation has been studied experimentally as a frequency conversion process for efficiently generating powerful output at near UV and visible wavelengths. Excimer lasers offer high peak powers and energies at a variety in ultraviolet (typical values are several hundreds of mJ from ArF-193 nm to XeF-351 nm). Unfortunately, the tunability of these systems is limited to only about 0.2 nm. For some applications Raman conversion helps to extend the range of available wavelengths to a more useful region where high powers are not readily available by other schemes.

The most commonly employed medium for Raman shifting is hydrogen gas because of its large vibrational shift and its low dispersion. Efficient Raman shifting of ArF, KrF,[1] and XeCl (Refs. 2 and 3) have been demonstrated several years ago. Most Raman conversion data in these experiments were obtained at single pulse or at low repetition rate.

In this communication we present the results of Raman experiments at high repetition rate up to 150 Hz. The experimental results show reduction of Raman conversion efficiency when the repetition rate of the pumping laser is increased in a sealed Raman cell. Improved Raman conversion efficiency is obtained by flowing the hydrogen gas at interacting region of the Raman cell. The excimer laser used as a pumping source is a commercial discharge-excited device (Questek 2240), which was operated with gas mixture containing 2.6% F2, 5.6% Kr, and the balance He at 2.7 bars. An unstable resonator was adopted for improving the beam quality. The laser produces average power of 25 W at 150 Hz with pulse length of 25 ns (FWHM).

The Raman system consists of a 0.6 m long cell and a specially designed hydrogen gas circulating pump. The Raman cell has two tilted windows; each window has two-face antireflected coating at 248 nm. The hydrogen gas pump was designed for circulating hydrogen gas at the focal plane in