Overcoming Cellular Breakdown in Hyperdoped Silicon Alloys

Brandon Piercy
Materials Science and Engineering, Case Western Reserve University

NNIN REU Site: Center for Nanoscale Systems, Harvard University, Cambridge, MA
NNIN REU Principal Investigator: Prof. Michael Aziz, School of Engineering and Applied Sciences, Harvard University
NNIN REU Mentor: Daniel Recht, School of Engineering and Applied Sciences, Harvard University
Contact: brandon.piercy@case.edu, aziz@seas.harvard.edu, drecht@fas.harvard.edu

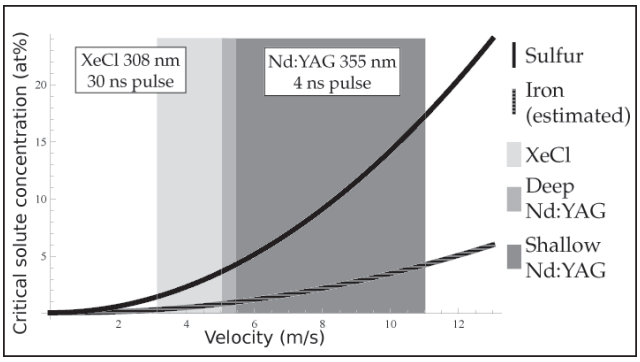

Figure 1: Minimum solute concentration of iron and sulfur in Si that can be achieved as a function of solidification velocity, calculated using parameters from [6], and accessible velocity regimes for different lasers. V_d = 10 m/s was used as an estimate for iron.

Abstract and Introduction:

Hyperdoped semiconductors, i.e. semiconductors that have been doped far above the solid solubility limit, represent a route towards high-efficiency, scalable, and low-cost solar cells and photodetectors [1]. Ion implantation followed by pulsed laser melting (PLM) has been demonstrated to be an effective method for hyperdoping semiconductors [2]. PLM-created alloys are currently limited in doping concentration by a phenomenon known as cellular breakdown: solidification front instabilities force the solute to come out of solution [3, 4]. This effect is primarily governed by the speed of solidification in the material as described by Hoglund, et al. (1998) [5, 6]. An increased solidification speed should be able to trap more impurities without inducing cellular breakdown, as shown in Figure 1. A faster, lower energy laser pulse will induce a steeper thermal gradient across the melted region, increasing the solidification rate. This work demonstrates that by increasing the solidification velocity from 3-5 m/s to 8 m/s, single-crystal sulfur-silicon (S-Si) alloys of a world-record 2 at% can be created.

Experimental Procedure:

Positive (*p*)-type silicon (Si) wafers were ion implanted with: $^{32}S^+$ at 45 keV to a concentration of 1×10^{16} cm^{-2} (shallow implant), $^{32}S^+$ at 90 keV to a concentration of 1×10^{16} and 3×10^{16} cm^{-2} (deep implant), and $^{56}Fe^+$ at 80 keV to a concentration of 1×10^{16} cm^{-2}. The implantation depth was calculated, using the standard Stopping and Range of Ions In Matter (SRIM) code, to be 100 nm for the 45 keV S sample and 300 nm for the 90 keV S and the iron (Fe) samples. Samples of each type were melted in air using a Continuum Surelite pulsed Nd:YAG laser (355 nm, 4 ns FWHM, and 8 ns total duration) with a single shot. Additionally, the deep-implant S and the Fe samples were irradiated four times with a XeCl excimer laser (308 nm, 25 ns FWHM, and 50 ns total duration). The deeply implanted S and Fe samples were irradiated using the Nd:YAG at 0.9-1.1 J/cm^2, while the shallow-implant S sample was irradiated using the Nd:YAGat 0.5-0.7 J/cm^2. Fluence calibration was achieved by irradiating a single-crystalline Si wafer, recording the melt duration through time-resolved reflectivity of a low-power Ar^+ laser (488 nm, continuous wave), and comparing the data to predictions from a one-dimensional heat flow simulation [4, 5]. Imaging was performed using a Zeiss Supra field emission scanning electron microscope (SEM).

Results and Discussion:

The 1×10^{16} cm^{-2}, 90 keV, S-implanted Si is known to not undergo cellular breakdown when melted with the XeCl laser, and therefore acts as a reference for determining whether breakdown has occurred. Electron backscattering diffraction has previously been used to verify that XeCl-shot Si implanted with 3×10^{16} cm^{-2} S and 1×10^{16} cm^{-2} Fe both undergo cellular breakdown. The surface structure of the Nd:YAG-shot Fe-implanted Si (Figure 2) closely resembles the Fe-implanted Si shot with the XeCl laser, implying that cellular breakdown still occurs with iron ions at 1 at%.

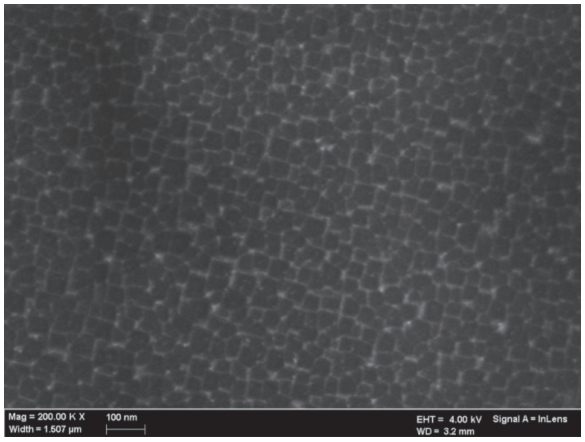

Figure 2: SEM image of Nd:YAG-irradiated Fe-implanted Si, showing clear signs of cellular breakdown.

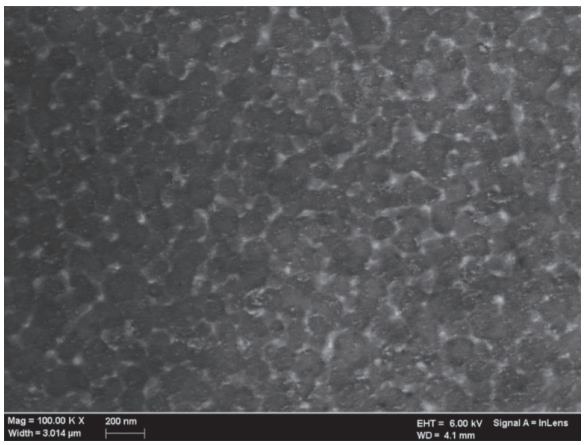

Figure 3: SEM image of Nd:YAG-irradiated, deep-implant S in Si at 3 × 10^{16} cm^{-2}, showing what may be cellular breakdown but with little periodicity.

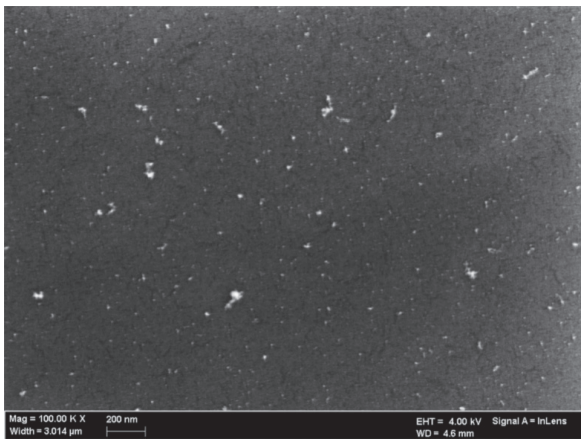

Figure 4: SEM image of Nd:YAG-irradiated shallowly-implanted S in Si. The white clusters and dark lines are not associated with cellular breakdown.

However, in the 3 × 10^{16} cm^{-2} S-implanted Si, there was significant variation between the microstructures created from the XeCl laser and the Nd:YAG laser. The pattern visible from the XeCl laser was periodic and on the order of 200-250 nm – unlike the surface structure created by the Nd:YAG laser, which was either a regular pattern on the order of 100-150 nm (Figure 3), or had no surface patterning. This indicates that this sample was at the point where minor variations in fluence across the laser beam were able to cause or prevent cellular breakdown.

Heat flow simulations indicated that the peak solidification velocity, and therefore the maximum solute concentration, could be achieved with a combination of a thin implant layer of 100-150 nm and laser fluence around 0.4 J/cm^2. The results from the shallow S-implanted, 1 × 10^{16} cm^{-2} Si sample, indicated no regular surface patterning, and were qualitatively identical to samples in which breakdown did not occur (Figure 4).

Pending verification from XTEM, this represents the first single-crystalline sulfur-silicon alloy above 2 at%. Future work will explore the creation of previously impossible hyperdoped alloys across a range of alloying elements.

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References:

[1] M.T. Winkler, D. Recht, M.J. Sher, A.J. Said, E. Mazur, and M.J. Aziz, Physical Review Letters, 106, 178701 (2011).

[2] B. Bob, A. Kohno, S. Charnvanichborikarn, J. Warrender, I. Umezu, M. Tabbal, et al., Journal of Applied Physics, 107, 123506-123506 (2010).

[3] J. Narayan, Journal of Crystal Growth, 59, 583-598, (1982).

[4] M. J. Aziz, C. W. White, J. Narayan, and B. Stritzker, in Energy Beam-Solid Interactions and Transient Thermal Processing, edited by V. T. Nguyen and A. G. Cullis (Editions de Physique, Paris, 1985), p. 231–236.

[5] R. Reitano, P. Smith, M.J. Aziz, Journal of Applied Physics, 76, 1518-1529 (1994).

[6] D. Hoglund, M. Thompson, M. J. Aziz, Physical Review B, 58, 189 (1998).