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# Strong mid-infrared optical absorption by supersaturated sulfur doping in silicon

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**Abstract.** Single crystalline silicon supersaturated with sulfur was prepared by ion implantation followed by pulsed laser melting and rapid solidification. A strong and broad optical absorption band and free-carrier absorption appeared for this sample around 0.5 eV and below 0.2 eV, respectively. A possible candidate for the origin of the 0.5 eV band is the formation of an impurity band by supersaturated doping.

**Keywords:** Pulsed laser melting, silicon, impurity band, supersaturation, sulfur, solidification, optical absorption
**PACS: 78.30.Am, 81.10.Dn**

## INTRODUCTION

The maximum concentration of impurity doping is limited under thermal equilibrium conditions. Pulsed laser melting (PLM) is one of the non-equilibrium methods that creates large dopant supersaturations in silicon.[1-3] Sulfur is known as a double donor for silicon with an equilibrium solid solubility of up to about $10^{16}$ $cm^{-3}$. Supersaturated dopant concentrations may reveal effects of high carrier concentrations or of metastable states. For example, the formation of a deep impurity band may lead to high-efficiency solar cells.[4] Sulfur supersaturated silicon has been prepared by ion implantation and PLM-induced rapid solidification, and a very strong and broad sub-bandgap optical absorption was observed in the near-infrared region.[5,6] In the present paper, the mid- to near-infrared optical absorption of the sulfur supersaturated silicon samples was measured in order to elucidate the nature of the absorption band.

## EXPERIMENT

Boron doped p-type Si wafers were ion-implanted with 95 keV $^{32}S^{+}$ to a range of fluences up to $1x10^{16}$ ions/$cm^2$. The ion-implanted samples were then irradiated with a pulsed $XeCl^{+}$ excimer laser beam of 308 nm. Further details on sample preparation procedures can be found in Ref. 5. The transmission spectra were measured by a UV-VIS-NIR grating spectrometer and FTIR spectrometer up to 2.5 μm and above 2.5 μm, respectively.

## RESULTS AND DISCUSSION

The depth profile of sulfur was measured by secondary ion mass spectrometry (SIMS), revealing a sulfur supersaturated surface layer (with a concentration above $10^{20}$ $cm^{-3}$ exceeding the solubility limit) about 250 nm thick. The crystallinity of the pulsed laser melted layer was confirmed by Rutherford backscattering spectrometry and ion channeling.

The value of $\alpha d$, where $\alpha$ is absorption coefficient and $d$ is effective thickness, is plotted as a function of photon energy in Fig.1. A very broad and strong absorption band is observed at around 0.5 eV for the sample with the highest dose and a shoulder was observed at around 0.4 eV for lower dose samples. The optical absorption coefficient, $\alpha$, of this band is in the order of $10^4$ $cm^{-1}$ at maximum. This absorption band was not observed in as-implanted samples, suggesting that such absorption originates in the supersaturated

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crystal. The dilute sulfur-related deep centers have been reported for non-supersaturated samples to be at 0.32, 0.61, 0.19 and 0.37 eV below the conduction band edge for $S^0$, $S^+$, $S_2^0$ and $S_2^+$ states, respectively.[7] The optical absorption peaks or shoulders corresponding to these centers were not present.

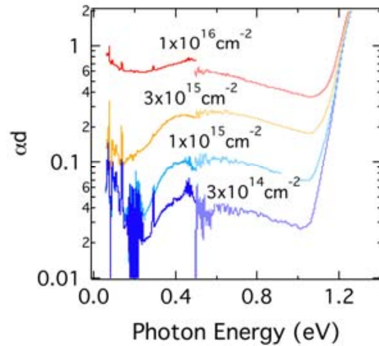


**FIGURE 1.** Optical absorption spectra of sulfur-supersaturated Si samples for 4 different implantation doses. The discontinuity at 0.5 eV is due to a switch in spectrometer.

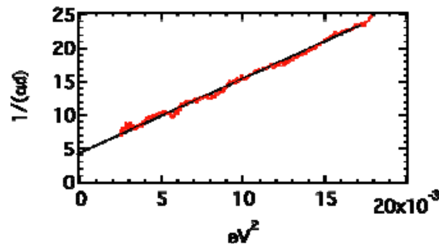


**FIGURE 2.** The value 1/αd plotted vs. the square of the photon energy for the sample implanted at $1x10^{16}cm^{-2}$.

We estimated the number of electrons, which contribute to the absorption band centered at around 0.5 eV, by Smakula's equation to be about $10^{21}$ $cm^{-3}$ for the sample with the highest sulfur concentration.[8] This value is of the order of the number of electrons supplied by sulfur ions. These results suggest that one of the possible origins of the strong and broad absorption band is the formation of an impurity band by supersaturated concentration.

An increase in the value of $\alpha d$ for photon energies below 0.2 eV is apparent. According to the Drude model, free carrier absorption is characterized by the following relationship between 1/α and photon energy:[9]

$$\frac{1}{\alpha}=\frac{\varepsilon_0 nc}{Ne\mu}+\frac{4\pi^2\varepsilon_0 cnm^{*2}\mu}{Neh^2}E^2 \quad (1)$$
,

where $N$, $e$, $\mu$, $m^*$, $\lambda$, $\varepsilon_o$, and $n$ are, respectively, the carrier concentration, electronic charge, electron mobility, electron effective mass, wavelength of light, free space permittivity, and refractive index. The value $1/\alpha d$ as a function of square of photon energy is shown in Fig.2. The plot shows a linear relationship below 0.02 $eV^2$(0.14 eV). The carrier density and mobility estimated by Eq.1 are ~$10^{19}$ $cm^{-3}$ and ~80 $cm^2$/Vs respectively. These values are consistent with those obtained by a Hall effect measurement.[10] These results indicate that the optical absorption below 0.2 eV is mainly due to free carrier absorption. The carrier density is about two orders smaller than the sulfur density. The temperature dependence of free carrier absorption was measured and, from the results, the temperature dependence of the carrier density was estimated. The activation energy was found to be below 100 meV. This suggests that carriers are activated not from all of deep absorption band but from only shallower part of the band at room temperature. This is consistent with the fact that the carrier to donor ratio is very small.

## CONCLUSION

A very strong and broad optical absorption band centered around 0.5 eV was observed by supersaturated doping with sulfur. Although the correlation between atomic structure around sulfur and this optical absorption band does not allow a definite conclusion, our results suggest that the formation of an impurity band by supersaturated doping is a possible candidate for the origin of this broad and strong absorption band.

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