Femtosecond laser hyperdoping and micro/nanotexturing of silicon for photovoltaics

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ABSTRACT

We have developed a technique, optical hyperdoping, for doping semiconductors to unusually high levels and endowing them with remarkable optoelectronic properties. By irradiating silicon (Si) with a train of femtosecond laser pulses in the presence of heavy chalcogen (sulfur, selenium, and tellurium) compounds, a 100-300 nm thin layer of Si is doped to non-equilibrium levels (~1 at. %). Hyperdoped silicon exhibits near-unity photon absorptance from the ultraviolet ($\lambda < 0.25$ μm) to the mid-infrared ($\lambda > 2.5$ μm), even though crystalline silicon is normally transparent to wavelengths $\lambda > 1.1$ μm due to its band gap at 1.1 eV. Concurrent to doping, we are also able to use fs-laser irradiation to create light-trapping surface textures on the micro- and nanometer scales. Together, optical hyperdoping and surface texturing represent a route towards high-performance thin film photovoltaic devices.

Keywords: intermediate band, photovoltaic, optical hyperdoping, femtosecond laser, silicon, chalcogen, surface texturing, light management

1. INTRODUCTION

For photovoltaic (PV) technologies to become preeminent, significant reductions in production cost must be achieved.[1] The three most important factors in reducing and stabilizing cost are: 1) increasing efficiency, thereby reducing all associated balance of systems costs concurrently; 2) reducing material requirements through scalable thin film technologies; and 3) using non-toxic and Earth-abundant materials to ensure sustainability. The femtosecond (fs) pulsed laser fabrication method we discuss here can potentially address these factors simultaneously. Efficiency improvements can be realized through the creation of an intermediate band via hyperdoping, which extends the device photoresponse range and thus the theoretical maximum efficiency (to >50% for Si)[2]. Additionally, material requirements are reduced due to concurrent surface texturing, which increases the light absorption of the device. Finally, the technique is versatile, as it can be applied to a wide range of Earth-abundant host materials and dopants. Here, we discuss our recent progress in fabricating intermediate band photovoltaics using ultrafast laser processing, focusing on both hyperdoping and surface texturing.

2. HYPERDOPING

Traditional semiconductor device fabrication methods give rise to dopant concentrations which are at or below the solid solubility limit. For example, the solid solubility limits of elements in silicon are often around 0.001 at. %. (except for group III, IV and V elements).[3] By using an 800-nm fs pulse train from a Ti:sapphire laser, shown schematically in Figure 1, we are able to incorporate dopants at concentrations thousands of times greater, near 1 at. %.[4,5] Such high concentrations are achieved through a process called solute trapping.[6,7] Laser pulses with energy greater than the melting threshold transform the surface into a molten layer, enabling dopant precursors in the vicinity to diffuse in. As the deposited energy diffuses into the substrate, the molten layer resolidifies with a speed greater than the rate at which thermodynamic equilibrium can be established (>1 m/s),[8] thus achieving supersaturated concentrations. The dopant precursors can be in the gas phase (such as SF_6) or the solid phase (such as thin films of Se or Te). The resulting high

Laser Applications in Microelectronic and Optoelectronic Manufacturing (LAMOM) XVII,
edited by Guido Hennig, Xianfan Xu, Bo Gu, Yoshiki Nakata, Proc. of SPIE Vol. 8243,
82431D · © 2012 SPIE · CCC code: 0277-786X/12/$18 · doi: 10.1117/12.908671

dopant concentrations give rise to an intermediate band — a swath of delocalized energy eigenstates located in the semiconductor bandgap.[9] By introducing an intermediate band via fs-laser hyperdoping, the host material's optical, electronic, and optoelectronic properties are drastically changed.

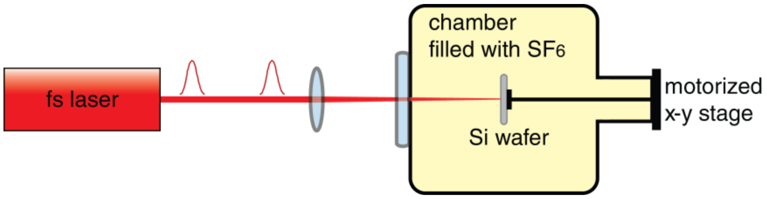

Figure 1 Schematic of fabrication setup for hyperdoped Si:S. To dope with Se or Te, thin films overlying Si are used as dopant precursors, and the sample is irradiated in an inert ambient gas such as nitrogen.

The effects of hyperdoping on the host material's optoelectronic properties depend on the dopant energy bands produced in the host material's bandgap. To guide dopant selection, the energy states produced in the dilute limit are often referenced as a first approximation of the states induced by hyperdoping (Figure 2). For photovoltaic applications, it is desirable to have the intermediate band isolated from the band edges and close to the mid-gap energy.[10] Furthermore, carrier excitation to or from the intermediate band is enhanced when the Fermi level resides within it. Below, we describe efforts to determine if an intermediate band is present after hyperdoping Si with chalcogens and, if so, what the properties of the resulting material are. (See Luque and Martí, 2010[11] for a thorough discussion of intermediate band photovoltaics.)

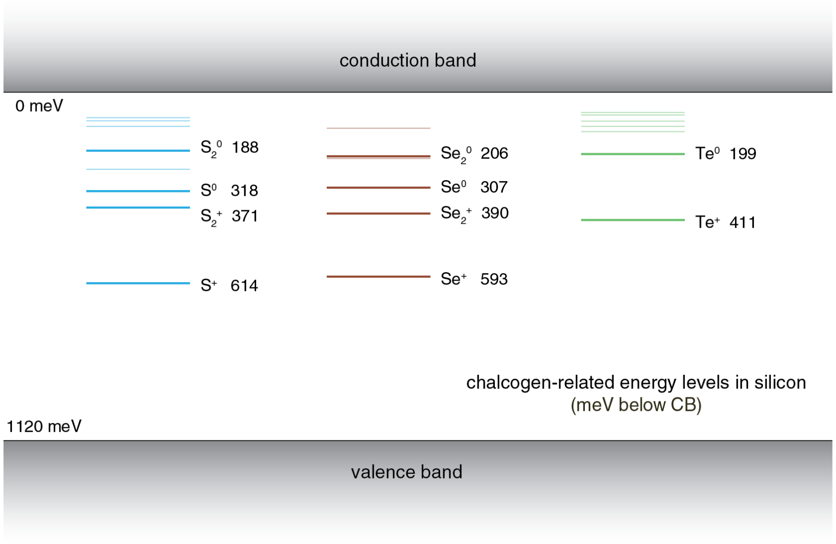

Figure 2 In the dilute limit, chalcogens produce deep-level impurities in silicon, suggesting they may be suitable for intermediate band devices. Adapted from references[12,13].

One of the most prominent characteristics of an intermediate band material is sub-bandgap optical absorptance due to excitations to or from the intermediate band. Hyperdoped Si shows enhanced sub-bandgap absorption from the bandgap energy to wavelengths > 2.5 μm, and when the surface is textured through fs-laser irradiation (see Section 3), the absorptance increases, approaching unity from < 0.25 μm to > 2.5 μm (Figure 3). As a measure of the ability to extract charge carriers excited by sub-bandgap light, the photoresponsivity[14] is shown in Figure 3. Though the photoresponsivity is enhanced at visible wavelengths due to light-trapping, the improved response does not extend far into the infrared. This relatively low sub-bandgap photoresponse could be due to fast recombination of intermediate band charge carriers; thus, for a photovoltaic device, improving the lifetime of these charge carriers is essential.

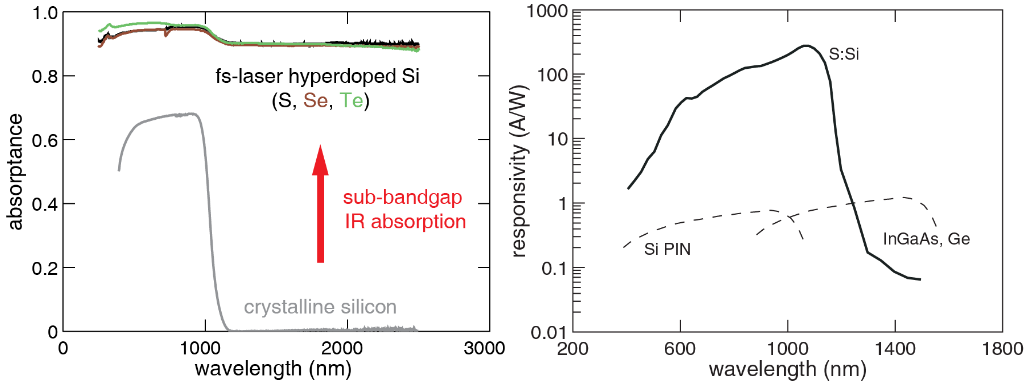

Figure 3 Left: Femtosecond-laser hyperdoped Si exhibits near unity absorptance from < 0.25 μm to > 2.5 μm. (Absorptance = 1 – R – T, where R and T are the measured reflectance and transmittance over all angles.) Sample was also fs-laser textured to increase its optical density. Adapted from Sheehy *et al.*, 2007.[5] Right: Spectral responsivity of hyperdoped silicon photodiode (S:Si) at −0.5 V bias. The responsivity data of a commercial silicon P-I-N photodiode and an InGaAs or Ge photodiode are shown for reference. Adapted from Carey *et al*., 2005[14].

To improve the material quality and thus the device performance, thermal annealing experiments were performed on hyperdoped Si.[14,15] Thermal annealing up to 1175 K improves the carrier transport but reduces the amount of infrared absorption.[15,16] This reduction in infrared absorption correlates with dopant diffusion out of the supersaturated solution to grain boundaries, where the dopant atoms can precipitate.[16] At higher temperatures, however, the sub-bandgap absorption is reactivated, as shown in Figure 4. If high temperature annealing ($T > 1350$ K) is followed by quenching (> 50 K/s), then the hyperdoped silicon's infrared absorptance is partially maintained. The fact that the sub-bandgap absorptance depends on the cooling rate suggests that the optical effect of the dopant is kinetically limited, and the effects of the dopant's local environment were recently invesitaged.[17] Beyond offering insight into the nature of the infrared absorptance in hyperdoped silicon, these results demonstrate that sub-bandgap absorptance can be thermally engineered and controlled to optimize device characteristics.

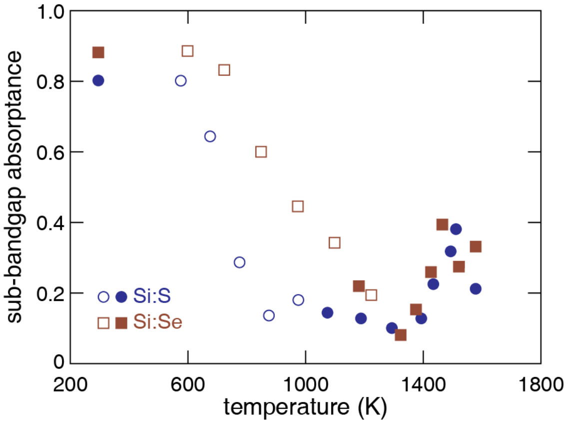

Figure 4 Reactivation of infrared absorptance. Average sub-bandgap absorptance (1.25 to 2.50 μm) for hyperdoped Si after annealing and quenching (cooling rate ~50 K/s).[15]

Finally, in order to probe the dopant energy levels and the occupation of the intermediate band, the temperature-dependent charge transport properties of hyperdoped Si:S were studied using Hall effect measurements. Sheet carrier concentrations derived from these measurements show that the concentration of n-type carriers is maintained at low temperatures (Figure 5), suggestive of metallic conduction.[18] Recently, hyperdoping with sulfur was reported to induce an insulator-to-metal transition in Si,[19] evidence that the dopant electron wavefunctions are, indeed, delocalized.

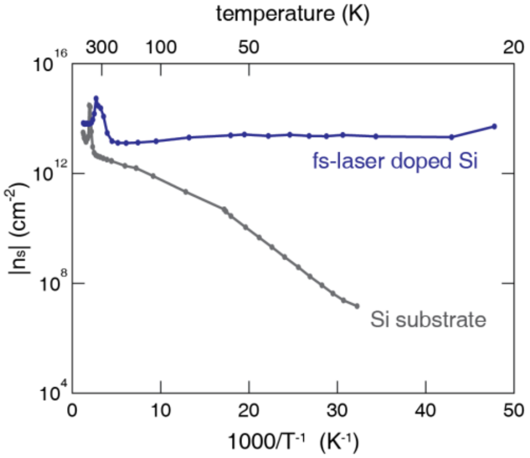

Figure 5 Sheet carrier concentration of sulfur-hyperdoped Si as a function of inverse temperature. The fs-laser doped Si maintains its concentration of n-type carriers at low temperatures.[18]

3. SURFACE TEXTURING

Femtosecond-laser texturing originates from the formation of laser induced periodic surface structures (LIPSS)[20,21,22] and consists of semi-periodic, nanometer- and micrometer-scale structures. These laser textured surfaces are independent of the crystal orientation and exhibit a wide range of feature sizes. LIPSS have been observed in a variety of materials and are caused by the interference of incident light with surface plasmon polaritons. They are often polarization dependent, such as the ripples shown in Figure 7, with a periodicity which is perpendicular to the incoming polarization. The period of the ripples is wavelength dependent; using a Ti:sapphire laser at a wavelength of 800 nm, we see ripples with a period of roughly 380 nm. Recently, we identified laser parameters for independently tuning the hyperdoping and texturing processes.[18,23]

Femtosecond-laser textured surfaces have excellent light-trapping and anti-reflective properties[24] (as shown in Figure 3), approaching the theoretical Yablonovitch light-trapping limit.[25] We have produced light-trapping structures on both crystalline and amorphous silicon and on both thin films and thick substrates[24] (Figure 6), indicating the potential for laser texturing in the photovoltaic industry. The ability of fs-laser irradiation to create highly effective light-trapping surfaces on thin films is particularly promising, as it reduces the required thickness of the active layer and thus the diffusion length necessary for charge collection. By tuning the laser parameters, a wide range of surface morphologies can be created, including specularly flat, rippled, and spiky, as shown in Figure 7.

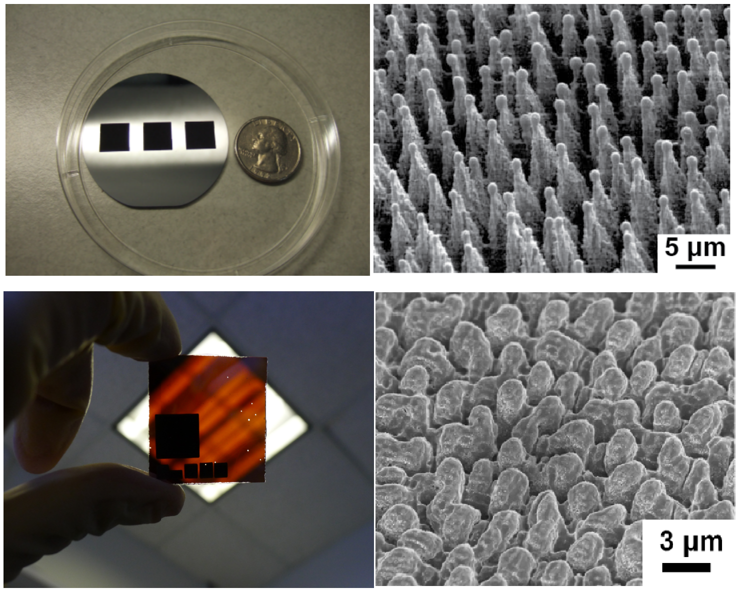

Figure 6. Light trapping by fs-laser surface texturing. Top: monocrystalline Si wafer with light-trapping surface cones shown in scanning electron micrograph (angled view).[20] Bottom: polycrystalline Si thin film on glass with light-trapping mounds (angled view).

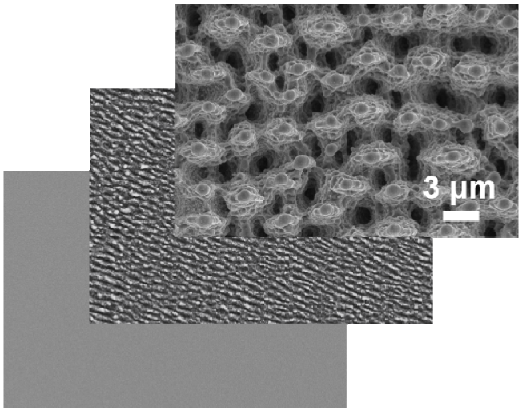

Figure 7 Scanning electron micrographs (top view) of selected surface morphologies obtainable with fs-laser processing using different irradiation parameters, including specularly flat, rippled, and spiky.

4. CONCLUSIONS

Ultrafast laser processing represents a potential route toward both high-efficiency photovoltaic concepts (such as the intermediate band solar cell) and improvements of existing photovoltaic technologies (such as the production of laser-induced light-trapping surface textures). Here, we have reviewed our recent progress in understanding the effects of optical hyperdoping and in developing light-trapping surface textures on bulk and thin film Si. Hyperdoping Si with heavy chalcogens results in sub-bandgap optical absorptance and optoelectronic responsivity, indicating the formation of an intermediate band. Although sub-bandgap photons with wavelengths greater than 2.5 μm are absorbed, the sub-bandgap photoresponse remains low, perhaps due to fast recombination of these carriers, and improving the carrier lifetime is a topic of current research. The connection between absorptance and thermal treatments indicates that dopants take on optically active and inactive states based on their local environments and that fast thermal quenching is required for high optical absorption.

Laser-induced surface textures trap light, significantly increasing the optical density of Si. Thus, fs-laser processing may be of particular value in the fabrication of thin film photovoltaic devices, where high optical densities are crucial for reducing the material requirements while preserving the photoconversion efficiency. A wide range of surface textures can be produced by changing the laser parameters and irradiation conditions. Together, optical hyperdoping and surface texturing by ultrafast laser processing comprise a route toward high-performance thin film photovoltaic devices.

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