

Research Letter

Observation of Quantum Confinement Effects with Ultrashort Excitation in the Vicinity of Direct Critical Points in Silicon Nanofilms

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We report on the observation of quantum confinement effects and the influence of surface-related states due to the formation of nanograins on ultrashort relaxation near the direct critical points of silicon nanofilms following UV-excitation. Direct photoexcitation of the samples in the vicinity of the Γ critical points of the first Brillouin zone has been achieved using femtosecond pulses in the spectra range of 290–400 nm. Transient absorption measurements show a substantial enhancement of state filling with decreasing the film thickness down to 5 nm due to quantum confinement in the z-direction. Furthermore, the state filling of surface-related states of nanograins suggests that the critical points of these states follow the ellipsometry extracted energy-curve.

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1. INTRODUCTION

Polycrystalline silicon is considered an important component of the silicon-based integrated-circuit technology and is currently utilized in a wide range of devices applications [1–3]. Driven by the promising technological applications of the polycrystalline silicon films, significant progress has been made in understanding the structural, electrical, and optical properties of this material [4]. However, little effort has been focused on ultrathin nanoscale polycrystalline films. At these thicknesses due to the large fraction of boundary-atoms and quantum effects imposed from the vertical structural confinement, the energy states of these nanofilms are modified [5–8]. A study of the optical properties under steady-state conditions using spectroscopic ellipsometry of such nanostructures have been recently published [9]. Based on the extracted information from that work, recently we have reported on carrier dynamics and the effect of grain boundaries and quantum confinement in these samples using visible ultrashort pulse excitation [10]. Although some interesting effects have been revealed, there still a great deal of unexplored area in the field of carrier dynamics especially when exciting in the UV part of the spectrum which is

energetically position near the Γ points (direct critical points) of the first Brillouin zone.

In this letter, we report on the observation of quantum confinement effects and the influence of relaxation dynamics near the Γ points of the first Brillouin zone due to the surface-related states surrounding the nanograins using transient absorption measurements. The samples investigated were nanocrystalline silicon films with thickness ranging between 30 to 5 nm. In our studies, we use UV photoexcitation, energetically located within the vicinity of the direct critical points of the first Brillouin zone. A direct consequence of this excitation is an enhance dipole matrix coupling as opposed to older studies where phonon-assisted excitation generated the initial carriers within the band structure of this material. In this work, we are able to time-resolve the relaxation paths within the complex energy structure of the nanofilms.

2. EXPERIMENTAL

The source of excitation consists of a self-mode-locked Ti:Sapphire oscillator-amplifier system generating 45 femtosecond pulses at 800 nm. An optical parametric amplifier provided wavelength tunable pulses in the UV part of

the spectrum in a typical noncollinear pump probe setup where the differential reflected and transmission signals were measured using lock in amplifiers. A small fraction of the fundamental pulse was used to generate super continuum white light by focusing the beam on a sapphire plate for nondegenerate measurements. The temporal variation in the absorption was extracted using the transient reflection and transmission measurements [11, 12] in the range of 290–400 nm. Measurements reveal that approximately 68% of the incident energy is absorbed by the thin films. There is a $\pm 5\%$ variation in the absorbed energy depending to the film thickness. In view of this, the incident fluences were adjusted to maintain a carrier density of approximately $\sim 1 \times 10^{19}$ carriers/cm³ for all the nanofilms. The samples under investigation were as grown nanocrystalline silicon films fabricated on a quartz substrate using LPCVD of silicon from silane at 610°C and 300 mTorr. High-resolution transmission electron microscopy images exhibit high degree of crystallinity for all samples, more structural detail on these samples are described elsewhere [9, 10, 13]. Spectroscopic ellipsometry measurements carried out on these samples [9] reveal the energy positions of the direct critical points Γ_1 (~ 3.5 eV) and Γ_2 (~ 4.2 eV) in the first Brillouin zone.

3. RESULTS AND DISCUSSION

Typical time-resolved absorption measurements for the nanostructured films are shown in Figure 1. It depicts the temporal behavior of the induced absorption following optical excitation at 300 nm. Clearly evident is the sharp drop of the induced absorption for the 5 nm film followed by a long recovery toward equilibrium. The observed negative change for the 5 nm sample is much larger than the observed negative changes for the 10 and 15 nm samples.

Time-resolved measurements for films with thickness larger than 10 nm appear to have complex behavior. They have negative and positive changes depending on the probing wavelengths and film thickness. For the thicker samples, there is a fast rise in the induced absorption which recovers within 10 picoseconds to a negative value followed by a much slower recovery toward equilibrium (\sim nanosecond). Similar effects occur at other excitation wavelengths.

In a simple semiconductor system following optical excitation, these carriers will lose their kinetic energy through optical phonon emission [12] and will relax to the bottom (top) of the conduction (valence) band. However, due to the complex nanostructure of these films, the presents of surface states [14], boundaries, and spatial confinement [15, 16] will effect the relaxation of the photogenerated carriers. The observed complex behavior in the above time-resolved measurements (Figure 1) is attributed to the position of the various energy states, their density and distribution with respect to the excitation energy (see inset in Figure 1). In a degenerate pump-probe experiment where the probing and excitation beams have the same wavelength, one expects to see negative change in absorption due to the occupation of the excitation/probing states by the photogenerated carriers. This effect, however, is usually noticeable under direct photoexcitation, seen mainly in direct gap semiconductors.

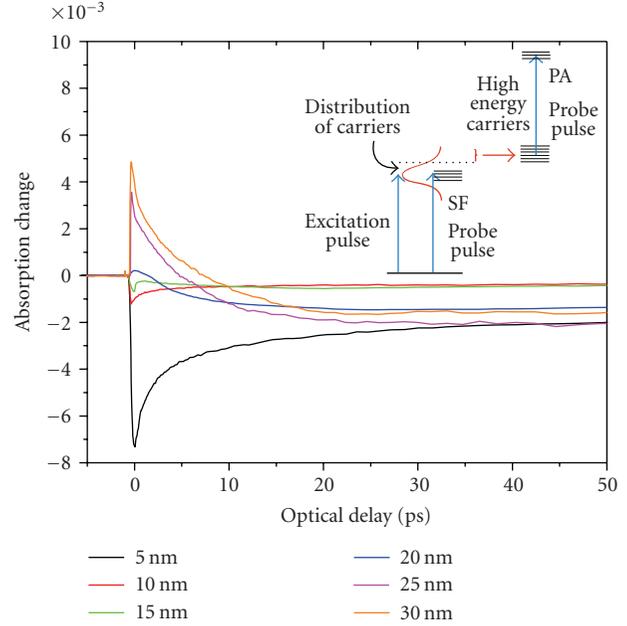


FIGURE 1: Degenerate time-resolved absorption measurements of the nanofilms with ultrafast UV excitation pulses at 300 nm. The inset shows a schematic representation of the carrier dynamics following photoexcitation.

In an indirect gap semiconductor like silicon this effect is highly unlikely due to the required phonon-assisted absorption. For this reason, in our work we use UV excitation where the photon energy may generate carriers near the vicinity of direct Γ points of the first Brillouin zone. We should point out that in addition to the above described state filling, there are also effects due to secondary excitations of the photogenerated carriers introduced by the probing laser pulse. With the relaxation of these carriers to various available energy states of the material, there is a possibility that the probing pulse will re-excite them to higher energy states if these are available. This mechanism will appear as a positive change in absorption (photoinduced absorption—PA) with its strength depending on the coupling efficiency (dipole matrix element) and the number of carriers presents in the initial energy state (see the inset of Figure 1).

The time-resolved measurements in the nanofilms reveal a complex behavior with both negative (state filling) and positive (PA) contributions present. The observed recovery of the state filling effect seen in the thinner sample can be expressed as a three exponential decay. The first two components are approximately 1 picosecond and 20 picoseconds. The third component to the decay is much longer and approximately 1 nanosecond. The first two components are a combination of redistribution of the initially photoexcited carriers within the states below the excitation level and secondary excitation resulting in “pulling” the signal above zero and artificially changing the decay constant. The long decay component is, however, a characteristic time for the energy states within the excitation region. The strong state filling which is only observed for the 5 nm thickness sample

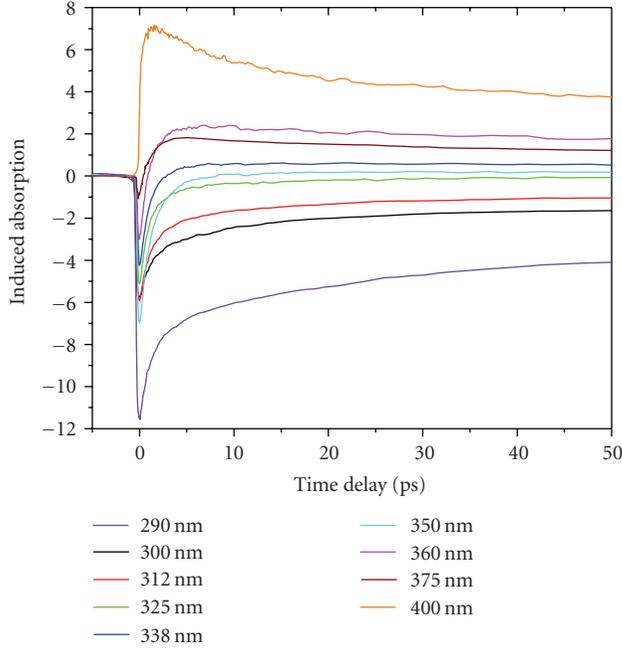


FIGURE 2: Time-resolved absorption measurements of the 5 nm film with UV excitation pulses ranging between 290 to 400 nm.

it is believed to be due to an enhanced coupling coefficient resulting from the spatial confinement in this sample. For comparison purposes, in Figure 2 we show the temporal behavior of the 5 nm thick sample for all the excitation wavelengths. It is obvious that state filling is the dominant effect for the shorter wavelengths; however, with increasing probing wavelength, PA becomes more important. This is clearly seen for wavelengths longer than 350 nm (3.5 eV, energy of the Γ_1 of the Si nanofilms) and at the longest excitation wavelength of 400 nm the only term apparent in the transient measurements is a positive PA contribution.

The fast PA behavior observed for the shorter wavelengths for the thicker samples (Figure 1) is attributed to the broad energy distribution of the pulse and the existing of various energy states near the excitation region (see inset in Figure 1). Following short pulse excitation, the carriers in the higher part of the energy distribution move to nearby energy states that provide efficient secondary excitations due to coupling with higher lying energy states. With energy relaxation of these carriers into other states, the contribution of secondary excitations to the induced absorption becomes negligible. At this point, state filling due to the rest of the photoexcited carriers becomes evident which persists for approximately 1 nanosecond. Since no measurable photoluminescence has been detected from these samples, the carriers appear to recombine nonradiative with time constant of the order of 1 nanosecond.

Looking at the data over the entire wavelength excitation range, it is interesting to point out that state filling is initially important for the nanofilms where the excitation is below the Γ_1 point (see Figure 3). This state filling is due to occupation of the surface states energetically located below the Γ_1 point

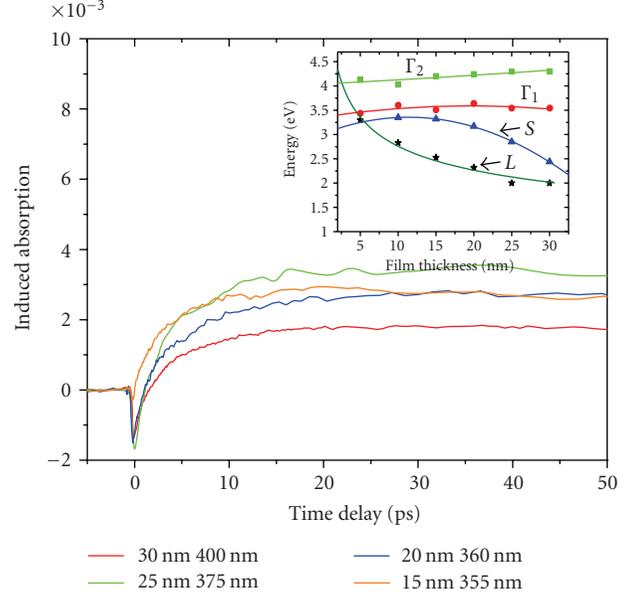


FIGURE 3: Degenerate time-resolved absorption measurements of the nanofilms where the apparent state filling is due to occupation of surface states located below the Γ_1 point. The inset shows the critical points for the nanofilms obtained using ellipsometry measurements [9].

as shown in the inset of Figure 3. With reduction of the film thickness, the surface states move energetically higher making state filling apparent at smaller wavelengths. Here, we should note that the surface state filling effect is much smaller in magnitude than the state filling observed for the 5 nm sample.

It is important to point out that the enhanced state filling due to the confinement in combination with the strong free carrier absorption observed at longer wavelengths is a property that may have direct application to optoelectronics for optical switching where a tunable laser above or below the Γ points will result in a positive or negative change in absorption. This is particularly useful since this property is observed in silicon which is the basis for our semiconductor industry.

Finally, to further investigate the relaxation dynamics for the thinner sample where quantum confinement effects become important, we have performed nondegenerated time-resolved measurements over the excitation range of 290–400 nm. Measurements reveal similar photoinduced absorption behavior over the entire excitation range. Typical time-resolved measurements with pump at 300 nm and probe with different white light wavelengths are shown in Figure 4. The smaller probing wavelengths have a positive contribution with multiexponential recovery toward equilibrium, whereas the longer probing wavelengths have a recovery which is much faster (~ 1 picosecond) and it is single exponential.

The analysis for the nondegenerated measurements is more complex than that for the degenerate case; however, one may draw some general conclusions. The fast relaxation seen for the long wavelength probing is attributed to the

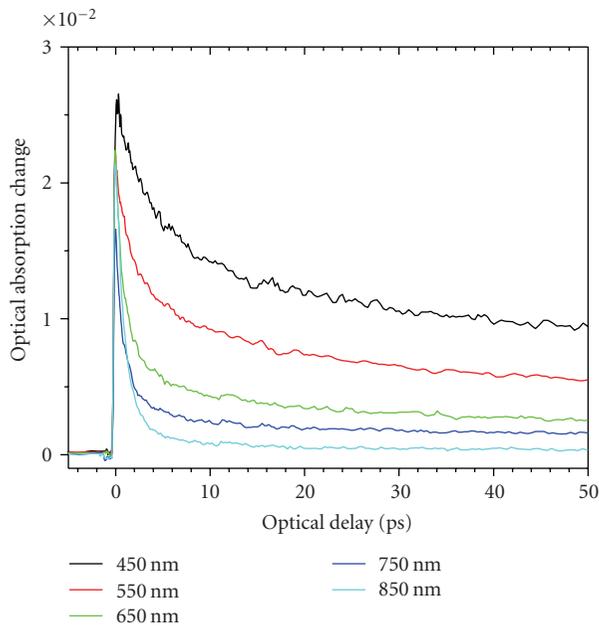


FIGURE 4: Time-resolved absorption measurements of the 5 nm film with 300 nm excitation pulses and probing with white light ranging between 450 to 850 nm.

relaxation of the carriers from populated states which couple to nearby higher energy states. These occupied states have a relatively fast relaxation as seen from the data in Figure 4 (see 850 nm). With increasing probing energy (shorter probing wavelength), the carriers available for coupling to higher states are distributed over a number of energy states each with a different relaxation rate. This makes the recover appear multiexponential. A satisfactory fit to the short wavelength data shown in Figure 4 has been achieved using a three exponential function. The time-resolved data for the 450 nm probing wavelength gave time constants of 3.2 picoseconds 17.5 picoseconds and 183 picoseconds with approximately equal coefficients. The fact that one observes longer recovery is attributed to the lower lying energy states where energy relaxation is slower.

4. CONCLUSIONS

In conclusions, we have utilized ultrafast UV laser pulses to investigate the photogenerated carrier dynamics near the vicinity of Γ points of the Brillouin zone of a set of nanofilms. We have observed state filling (negative change) and photoinduced absorption (free carrier absorption—positive change) as competing effects in the transient absorption of these nanofilms. State filling becomes enhance in ultrashort timescales for the smaller thickness samples where quantum confinement begins to play an important role. Furthermore, we have observed that the photogenerated carriers remain within the excitation states for a relatively long period of time. This was confirmed through state filling and free carrier absorption changes.

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