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Light from porous silicon by multiphoton vibronic excitation

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We study the emission of photons from porous Si after high-level vibrational excitation in the Si-O absorption band using a pulsed CO_2 laser. Narrow resonances in the efficiency of light generation are discovered at 1030 and 1084 cm^{-1}. Time-resolved experiments on the luminescence and the ir-induced changes in optical transparency show that the two excitation modes are characterized by different temporal responses. Additionally, their spectral distributions differ substantially. For excitation at 1030 cm^{-1} the familiar photoluminescence band of porous Si appears. We suggest microscopic processes responsible for the light emissions.

One of the most interesting effects in nonlinear optics is the phenomenon of infrared (ir) multiphoton excitation (MPE) and dissociation of molecules. It is possible to generate visible light by focusing a powerful pulsed CO_2 laser in a resonantly absorbing gas medium.[1] The effect is caused by selective absorption of several ir photons. This leads to a strong excitation of the molecule and, as a result, its possible dissociation and the emission of light. This method has been applied to study the interaction of intense ir fields with a multilevel quantum system. The distribution of the vibrational states for a highly excited molecule, the energy transfer between them, and the relaxation processes have been investigated.[2]

Energy transfer and relaxation processes are also of major interest in the field of surface physics.[3] The behavior of excited molecules absorbed on different solid substrates have been widely investigated. For metallic substrates, a strong coupling between the vibrating dipole and the electron gas results in fast relaxation.[4] On semiconductors, the coupling to the electronic system is usually weak. The energy transfer from the Si-H stretching mode on (111) Si has been studied. Relaxation occurs via coupling to surface phonons.[5] It is relatively slow compared to relaxation on metals, but still in the ns range,[6] much faster than the μs times observed for MPE in gases.[7] The fast relaxation is the main reason that MPE has never been observed in solids.

In this work we report on the observation of MPE and light emission via the excitation of the Si-O stretching vibration at the surface of Si particles in porous Si. To the best of our knowledge, this is the first report on such a mechanism operating in solids. We find that the Si-O vibration has a relatively long lifetime of the order of μs, and we identify the relaxation mechanism.

We used porous Si to study the excitation and relaxation properties of Si-O bonds. The huge surface area of the material ($\sim 10^7$ cm^2 per cm^3), allows for a large concentration of Si-O bonds on one hand, while on the other hand these bonds are spatially separated. This reduces the energy transfer between the oscillators, thus simulating the conditions found in gases.

The microporous Si samples are prepared by electrochemical etching of p-type (2–5 Ω cm), (100)-oriented Si wafers. The electrolyte is a 1:1 mixture of pure C_2H_5OH and concentrated aqueous HF. Typical thicknesses of the porous Si layer are 2–5 μm (for materials that remain on the substrate). We use free-standing layers (thickness ~ 20 μm) for the phototransmission experiment. The samples are oxidized by heating in air at 200 °C for various times in order to produce a given degree of oxidation.

For the experiments, the sample is mounted in a chamber, evacuated to ~ 1 mbar. The high-power ir pulses are provided by a transversely excited atmospheric (TEA) CO_2 gas laser tunable in discrete steps from 926 to 1087 cm^{-1}. The pulse width is ~ 150 ns in the primary peak, followed by a low intensity tail for about 2 μs. The incident ir intensity on the sample is controlled by inserting calibrated CaF_2 absorbers. In order to cut visible and near infrared light the pulse enters the chamber through a thick Ge window. Its intensity on the sample is monitored with a photon-drag detector. The luminescence is recorded with two fast detectors, a photomultiplier for the visible and near infrared spectral range, and a Ge detector for the infrared. With the photomultiplier, the system has a time resolution of 5 ns. All measurements are carried out at room temperature. The photoluminescence spectra are corrected for the spectral response of the optical system.

The dominant sample response to the ir pulse is a very

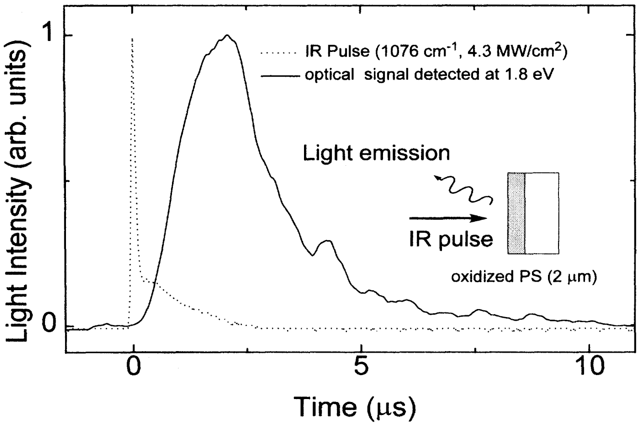

FIG. 1. The temporal behavior of the optical signal detected at 1.8 eV (solid line). The dotted line shows the shape of the ir excitation pulse (1076 cm^{-1}, 4.3 MW/cm^2).

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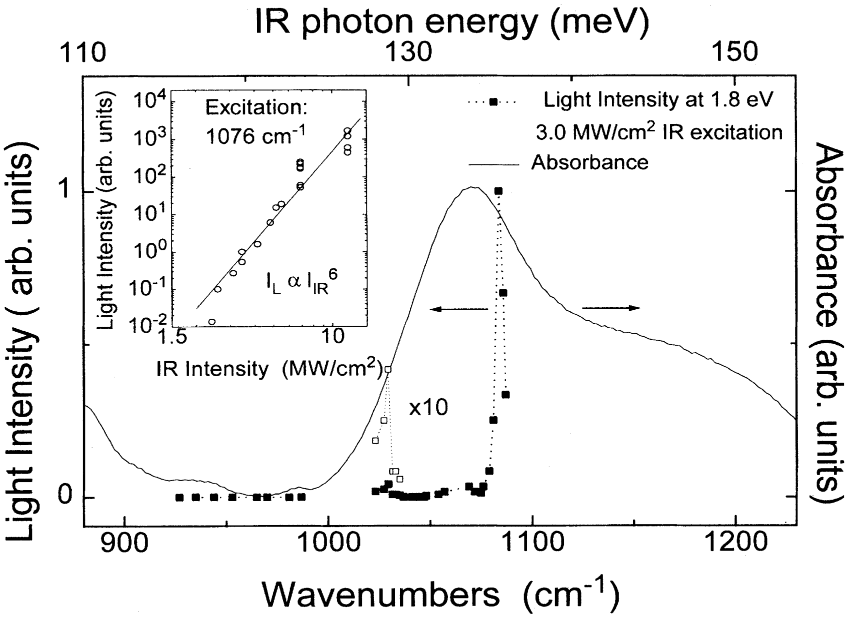

FIG. 2. Light emission at 1.8 eV as a function of the ir photon energy ($I_{ir}=3$ MW/cm^2). The solid line represents the ir absorbance of the porous Si layer. Inset: the magnitude of the optical signal versus ir pulse intensity (at 1076 cm^{-1}) with $I_L \propto I_{ir}^6$ (solid line).

weak luminescence extending in time for ~ 10 μs. It is possible to detect emitted photons with energies up to 2.4 eV. This corresponds, taking into account the energy of one exciting ir photon (0.133 eV), to more than 17 incident ir quanta. In Fig. 1, the temporal response of the emitted visible light detected at 1.8 eV is shown (solid line). The dotted line is the exciting ir pulse (1076 cm^{-1}, 4.3 MW/cm^2). The luminescence signal rises throughout the entire period of the ir pulse (~ 2 μs). Thereafter, it decays exponentially with a time constant of ~ 2.5 μs. The rise and decay shown in Fig. 1 are identical for all ir intensities from 1 to 6 MW/cm^2. They are independent of the detection energy over the range accessible for the fast photomultiplier (1.4–2.4 eV). With respect to the exciting ir intensity, the quantum efficiency of the visible light generation is extremely low.

To gain additional information on the excitation process that leads to the light emission we study the luminescence-excitation spectrum (Fig. 2). The emission at 1.8 eV is recorded (left axis, filled squares) for a constant ir pulse intensity of 3 MW/cm^2, while scanning the photon energy step by step through the modes of the CO_2 laser. The solid line shows the absorbance [measured by Fourier transform infrared spectroscopy (FTIR)] in the Si-O stretching-mode (between 1000 and 1250 cm^{-1}) from the partially oxidized internal surface layer of the porous Si. The material, characterized in Fig. 2, is only weakly oxidized and shows in the FTIR spectrum all H-related vibration modes.

An excitation within the broad Si-O absorption band results always in the generation of light. Nevertheless, it is possible to resolve a structure in the efficiency of light generation. Two sharp peaks, at 1084 cm^{-1} and at 1030 cm^{-1}, appear. The secondary maximum at 1030 cm^{-1} is shown in Fig. 2, enlarged by a factor of 10 (open squares). The sharp luminescence-excitation peaks are not present in the absorption, neither in the absorbance curve (see Fig. 2) nor in measurements of the absorption of the high-power ir pulses.

One possibility to account for the sharp response is the strong nonlinearity of the emission process. The inset in Fig. 2 shows that the luminescence intensity rises nonlinearly with the excitation intensity, following $\sim I_{ir}^6$ dependence when excitation occurs at 1076 cm^{-1}, at the low-energy side of the main peak. The same dependence applies at the peak itself. Nevertheless, even taking into account this nonlinearity, the 1084 cm^{-1} peak at the luminescence-excitation spectrum does not follow the absorption curve. To clarify whether the Si-O bond is related to the light emission we use a series of samples with increasing degree of oxidation. The visible luminescence excited at 1076 cm^{-1} is absent when no Si-O bonds are present. It rises with the oxide content but then vanishes when the surface of the Si particles is strongly oxidized. Thus, for high enough Si-O concentration the luminescence disappears. These results, combined with the sharp peak observed in the luminescence-excitation spec-

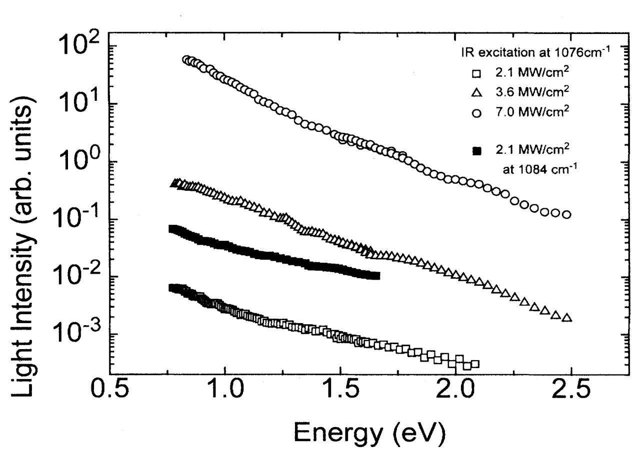

FIG. 3. ir-induced luminescence spectra at different excitation intensities for two different ir photon energies.

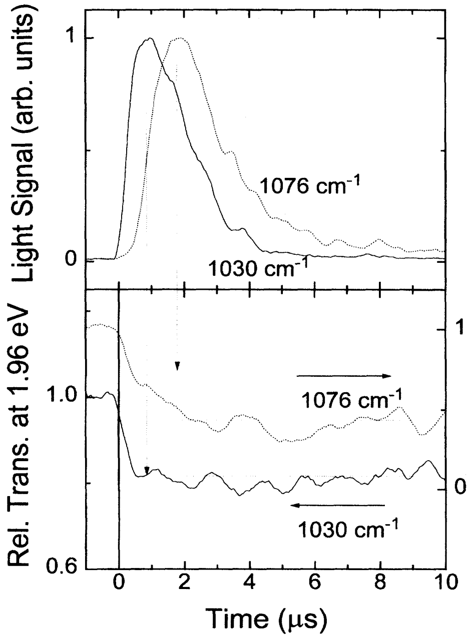

FIG. 4. Upper part: Time dependence of the optical response at 1.8 eV. ir excitation: 1030 cm^{-1} (solid line) and 1076 cm^{-1} (dotted line). Lower part: Optical transmission at 1.96 eV after ir excitation at 1030 cm^{-1} (solid line) and 1076 cm^{-1} (dotted line).

trum, suggest that the radiative source is an isolated atomic configuration on the surface of the Si particles.

Figure 3 gives the spectral distribution of the light emission. It is a broad, featureless, monotonic decrease. The decay is approximately exponential, but can equally well be fitted empirically with a relation like C^{-n}, where C is a constant and n the harmonic number at the emission energy. If we describe this distribution as a Boltzmann tail emitted from a black-body source its effective temperature would have to be of the order of 3000 K. For that temperature, the usual black-body Planck distribution would have a maximum in the spectral range investigated. Moreover, in a thermal model in which a black-body source is heated by the incident pulse, its effective temperature and therefore the emission spectrum should depend on the pulse energy. For incident intensities between 2.1 and 7.0 MW/cm^2, there is no change of the exponential slope, although the intensity of the emitted radiation increases by orders of magnitude. This behavior cannot be explained based on a thermal model.

We turn now to the second peak observed in the luminescence-excitation spectrum in Fig. 2. This resonance around 1030 cm^{-1} is a different mode of excitation. In the upper part of Fig. 4, the two ir excited luminescence kinetics are shown side by side. The emission for the 1076 cm^{-1} excitation has a slower rise time. It appears as the energy of the laser pulse (cf. Fig. 1) is accumulated over its full 2 μs duration. The maximum is reached at the end of the ir pulse. It decays with a time constant of 2.5 μs thereafter. Quite contrary, the 1030 cm^{-1} excitation causes the luminescence to appear concurrently with the ir pulse. It peaks below 1 μs and decays with a time constant of 1.4 μs.

The lower part gives the change of optical transparency of a free-standing, 20 μm thick porous layer for the red line of a He-Ne laser (1.96 eV) following the ir excitation. The transmission of porous Si at 1.96 eV is determined by the absorption of the Si particles. When the extra energy supplied by the ir pulse is transferred to the Si crystallites, they are heated. Because Si is an indirect semiconductor, an increase of the temperature will result in an increase of the absorption and a reduction of the transmission as observed in the experiment.

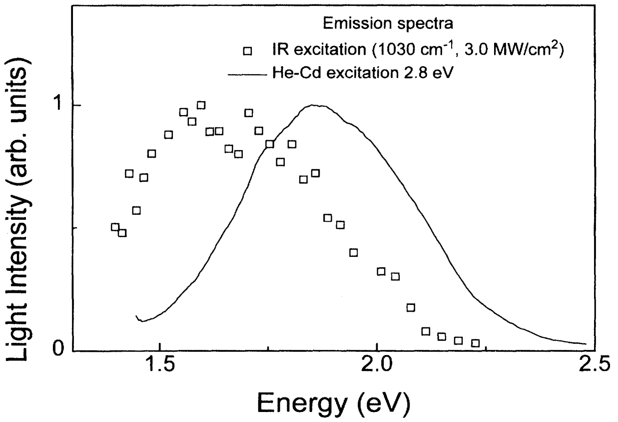

FIG. 5. Photoluminescence spectrum excited at 2.8 eV (solid line). Squares: spectrum of the light emission excited with 1030 cm^{-1} (3.0 MW/cm^{-1}).

For the 1030 cm^{-1} excitation, both the luminescence and the change in the transparency show the same fast rise time. Obviously for this case, the absorbed energy is quickly transmitted into the Si core. For the 1076 cm^{-1} excitation a slower energy transfer process takes place. It appears that the light emission rises as long as the energy is not fully transferred to the Si framework. After all the energy is transferred a decay of the luminescence is observed.

These results also show that the light emission is not directly related to heating. The temperature dependent transparency change has been calibrated in dc experiments.[8] The observed ~ 20% decrease of the transparency after the pulse is applied represents heating up to 120 °C above room temperature. The transmission fully recovers when the heat is dissipated after ~30 ms, much longer than the μs time scale of the emitted light.

The fast coupling of the vibrational energy to the Si core in the case of the 1030 cm^{-1} excitation manifests itself in the spectrum of the emitted light (Fig. 5). Irradiation at 1030 cm^{-1} leads to generation of visible light, which has a peak at 1.6 eV, and whose spectral distribution follows more or less the usual photoluminescence of porous Si. Evidently, this mode of excitation leads to a different channel of radiative relaxation. The difference in peak position for the luminescence excited with the 1030 cm^{-1} ir radiation (1.6 eV) and that of the conventional photoluminescence mode (1.8 eV), can be partially attributed to the increased temperature. A sample temperature of ~ 120 °C corresponds to a redshift of the luminescence peak position of about ~ 100 meV.[9] Furthermore, since the luminescence band is inhomogeneously broadened (due to particle size distribution) one would expect that the ir radiation would preferentially excite large particles, thus leading to a shift of the luminescence towards lower energies.

We now discuss the microscopic origin of the emitted light. The absorption of the ir photons by the Si-O bonds will result in an oscillation of these vibration modes. It is possible to describe an excitation mechanism similar to infrared multiphoton excitation of vibronic modes in molecules.[2] The lowest vibronic states of a molecule are discrete and the oscillator is anharmonic in nature. But starting from the 3–6 vibrational level, most molecules form a quasicontinuum of states. At high laser intensities effects like power broadening of the vibrational levels could lead to a reduction of the frequency mismatch between the low lying states of the vibronic ladder, allowing some bonds to be excited to the quasicontinuum. After reaching there further excitation is easy, because the density of the vibrational levels is rather high, and the infrared photon energy almost always coincides with a vibrational transition. Thus, intense infrared radiation can excite the Si-O bond to a high-energetic level, sufficient for the emission of light.

An essential requirement for exciting to the high levels is that the lifetime of the excited bond is comparable to the pulse duration. Both the luminescence and the induced transmission measurements show a slow μs type response (for the 1084 cm^{-1}). As a result, some bonds will stay excited for a long time and have a small but finite probability to reach highly excited states. The reason that the Si-O bond has such a long lifetime is the weak coupling between the oscillator and its surrounding. From the spectrum (Fig. 3), in particular the lack of the red peak, we realize that this vibration mode does not couple to the electronic states responsible for the porous Si photoluminescence. Furthermore, the excitation via MPE and dissociation is weak (the efficiency of the process is very low). The energy cannot diffuse along the surface, because the excited bonds are spatially isolated. The main relaxation mechanism is coupling to the phonon branches of the Si core, as evident from the heating of these Si particles. However, this process is slow, since in order to dissipate the energy of one ir photon, at least three phonons should be emitted. The slow response, the very high level of excitation, and the fact that there is no peak in the absorption lead to the suggestion that the radiative center is an isolated structural, Si-O related atomic configuration, of which there exist very few in the disordered, surface passivating, oxihydride layer.

Since the 1030 cm^{-1} mode heats the nanocrystals instantaneously, it represents intimate coupling of the primary local phonon excitation to the Si vibrations. One such possibility is a two-phonon Si-Si vibration process at the interface of the crystallite with the passivant. The energy is close to the value known from resonant second order Raman scattering in Si.[10] A matching of the phonon mode assures an efficient transfer of energy. The fast heating injects trapped carriers into the crystallites, as in a thermoluminescence process. The generated electron-hole pairs decay with the dynamic typically observed for photoexcited porous Si. The lifetime of 1.4 μs is in agreement with photoluminescence decay times in heated nanocrystallites.[9]

In conclusion, the experiments are the first indication that it is possible to create visible luminescence from a semiconductor by a multiphoton excitation process through vibrational states. The process is possible because porous Si, due to the huge surface area, is a material with a relatively high concentration of *isolated* Si-O bonds. This leads to a long relaxation time of the highly excited Si-O vibration, of the order of a few μs. For the special case of the two-phonon resonance, a faster relaxation is observed, and the emission characteristics are similar to that of the usual porous Si luminescence.

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