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Subthreshold photodissociation of H_2 in silicon

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A photodissociation of interstitial H_2 and D_2 in single-crystalline Si by a laser field at 532 nm is reported. It is shown that in the course of Raman scattering measurements with a power density of around 2×10^6 W/cm^2 the $H_2(D_2)$ signal decreases with a characteristic time of a few minutes. At temperatures below 100 K the molecule transforms into a metastable state known as H_2^*, which includes one hydrogen atom located at the bond-centered site and the second one at the antibonding position along the same $\langle 111 \rangle$ direction. At temperatures above 100 K both dimers dissociate, whereby the products of fragmentation, inaccessible for the Raman scattering, are proposed to be atomic interstitials.

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I. INTRODUCTION

Photodissociation is a process of fragmentation of a molecule through absorption of one or more photons. It is at the heart of photochemistry and plays a fundamental role in interstellar clouds, planetary atmospheres, and plasma physics [1,2]. In addition to its practical importance, photodissociation is a means to study molecular dynamics such as energy transfer between the various molecular modes, the breaking of chemical bonds and the creation of new ones, and the transitions between different electronic states.

In spite of its "simplicity," the hydrogen molecule (H_2) has fundamental importance in quantum mechanics, molecular physics, and chemistry. Since the pioneering work of Hopfield in 1930 [3], light absorption by molecular hydrogen became a subject of significant research interest [4–9]. Because the closest dipole allowed electronic transition lies 10 eV above the ground $X\,^1\Sigma_g^+$ state, all optical excitations leading to photodissociation of H_2 require either a single UV photon or multiple photons of less energies. The latter mechanism demands significant power densities ranging from 10^{11} to 10^{15} W/cm^2 [10–12].

By contrast with these well-known scenarios, here we report the results on photodissociation of H_2 in silicon by the visible light with power densities at least five orders of magnitude below those employed to break up the covalent bonding of hydrogen in the gas phase.

Molecular hydrogen was predicted to be stable in Si nearly four decades ago [13,14]. It took, however, 15 years until H_2 was observed experimentally [15,16]. In a defect-free lattice, H_2 occupies a tetrahedral interstitial T site and behaves as a nearly free rotator [17–21]. This results in two stretching vibrational modes at 3619 and 3627 cm^{-1} originating from ortho (nuclear spin 1) and para (nuclear spin 0) states, respectively [21]. Because of the symmetry requirements for the total wave function, only odd values of the rotational quantum number are allowed for ortho-H_2, whereas for para-H_2 they have to be even. The conversion between the two species is an extremely slow process. It takes weeks at 77 K until the ortho and para states come to a thermal equilibrium [22,23].

II. EXPERIMENTAL DETAILS

Here, photodissociation of interstitial H_2 in Si was observed in the course of Raman scattering measurements performed in a pseudo-backscattering geometry using the frequency doubled continuous wave 532-nm (2.33 eV) line of a Nd:YVO_4 laser. For this wavelength, the estimated probing depth in Si (band gap 1.12 eV) was about 0.4 μm [24]. The incident laser beam (spot size of around 20 μm) made an angle of 40° with the sample normal. The excitation power was varied between 0.5 and 1 W, i.e., estimated power density of 2×10^6 W/cm^2.

The Raman scattering spectra were recorded in a series of "frames." Each frame had a duration of 1 min, whereby the number of frames taken at *the same* excitation spot was 10 and 30 for hydrogen and deuterium treated silicon samples, respectively. The resulting spectra were averaged over *different* excitation spots.

The backscattered light was analyzed using a single grating spectrometer and a liquid nitrogen cooled Si CCD detector array. The spectral resolution was 2 cm^{-1}. The measurements were performed with the sample mounted in a cold finger cryostat using liquid helium for cooling.

Two p-type silicon (100) wafers were employed in this study: Czochralski-grown Si (Cz Si, oxygen concentration around 10^{18} cm^{-3}) with a resistivity of 45 Ω cm and float zone Si (FZ Si, oxygen-free) with a resistivity of 0.3 Ω cm. The samples were hydrogenated or deuterated for 30 min in a remote dc plasma at 230 °C [21].

During the measurements, the temperature in the bulk of the sample could be varied by an electrical heater. The actual temperature within the excitation area was determined from the Stokes to anti-Stokes ratio of the Γ-phonon line at 522 cm^{-1}. This allowed reliable temperature control down to

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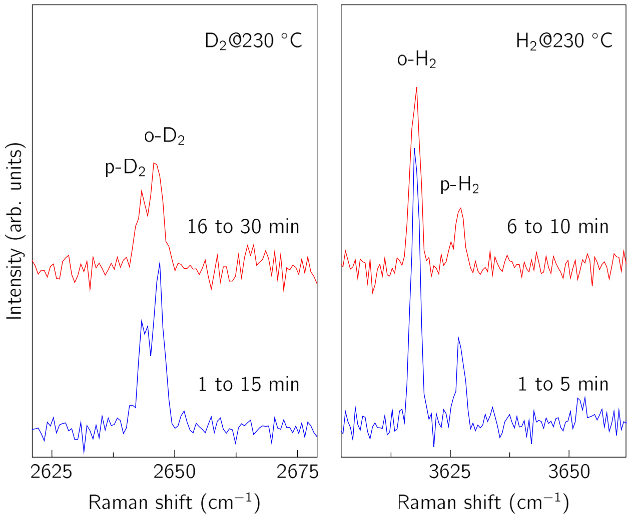

FIG. 1. Sections of Raman scattering spectra taken at nominally 4.5 K for FZ Si samples treated in the deuterium (left) and hydrogen (right) plasma at 230 °C. Excitation power was 1 W. The bottom and top spectra were averaged over the first and last 5(15) mins of the measurement time, respectively

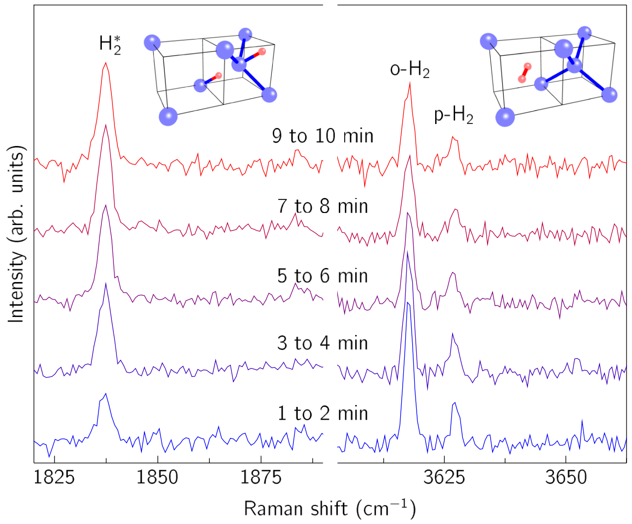

FIG. 2. Sections of Raman scattering spectra taken at nominally 4.5 K for a FZ Si sample hydrogenated at 230 °C. Excitation power was 1 W. The inserts sketch microscopic structures of H_2^* (left) and H_2 (right). Blue: Si; red: H.

approximately 70 K since, for lower temperatures, the anti-Stokes signal was too low to be determined with certainty.

III. RESULTS AND DISCUSSION

Figure 1 shows sections of Raman scattering spectra taken at nominally 4.5 K for two FZ Si samples treated in the hydrogen (right) and deuterium (left) plasma. In each case the spectra reveal a pair of lines due to vibrational modes of the interstitial molecule. The lines at 3619 and 3627 cm^{-1} are due to ortho- and para-H_2, respectively, whereas those at 2642 and 2645 cm^{-1} originate from para- and ortho-D_2. The relative intensities within each pair of lines (3:1 for H_2 and 1:2 for D_2) correspond to the ratio of their nuclear spin degeneracies [21,23]. The bottom and the top spectra in the figure were averaged over the first and last 5(15) mins of the measurement, respectively. Surprisingly, the Raman signatures of both H_2 and D_2 weaken with the measurement time. For each isotope the signal decreases down to about 60% of its initial value after exposure to the laser light for 5(15) minutes.

We emphasize that of all features occurring in the Raman spectra only interstitial H_2 turned out to be unstable with the measurement time. The Γ-phonon line at 522 cm^{-1}, H_2 trapped in platelets [25,26], or Si–H units forming the 2100-cm^{-1} band [16] were found to be time independent regardless of the sample temperature or laser power. Moreover, the stability of the Γ-phonon line strongly indicates that the excitation density remains below the damage threshold of silicon (see, e.g., [27]).

To account for such an unexpected behavior of the interstitial molecule at cryogenic temperatures, we consider first an out-diffusion of H_2 from the probing region into the bulk of the sample. From the known diffusion coefficient $D = 2.6 \times 10^{-4} \times \exp(-0.78\ \mathrm{eV}/kT)\ \mathrm{cm}^2/\mathrm{s}$ [28], one gets that it would take 10^{30} years at 80 K for the molecule to reach the next interstitial T site, which seems to rule out the out-diffusion as a mechanism explaining our findings.

On the other hand, one may argue that the laser excitation focused onto a small spot with a diameter of 20 μm significantly reduces the diffusion barrier of H_2. To verify this possibility the same measurements were repeated for Cz Si. In such a material H_2 left at room temperature for about an hour will diffuse through the sample and form complexes with interstitial oxygen [20,21,29]. Yet the decay of the interstitial molecule in Cz Si at cryogenic temperatures was not accompanied by the corresponding enhancement of the 3723, 3729, and 3736 cm^{-1} lines of the O-H_2 complex [21]. Such a result does not support the illumination-enhanced diffusion as a model explaining the instability of H_2 in the course of the Raman measurements.

Figure 2 shows Raman scattering spectra expanded to the region around 1850 cm^{-1} in comparison with the right panel of Fig. 1. The expansion of the spectroscopic region provides a necessary insight into the pathway of the H_2 evolution. As can be seen, the Raman signal of the molecule is anticorrelated with a 1838-cm^{-1} line originating from a stretch vibration of another hydrogen dimer known as H_2^* [30,31]. It consists of one hydrogen atom located close to the bond-centered site (H_{bc}) and the second one positioned at the antibonding (H_{ab}) site along the same $\langle 111 \rangle$ direction (see insert in the figure). Together with the 1838-cm^{-1} mode, H_2^* has a stretch and a wag mode at 2062 and 817 cm^{-1}, respectively (not shown).

Figure 3 presents integrated intensities of both hydrogen dimers obtained at nominally 4.5 K as a function of time. The excitation power was chosen to be 0.5 (left) and 0.75 W (right). It follows from the figure that the laser light is a decisive factor for the transformation of H_2 into H_2^*. On the other hand, the sample temperature within the excitation spot also depends on the excitation power. Since the actual temperature at nominally 4.5 K was not known, the same measurements

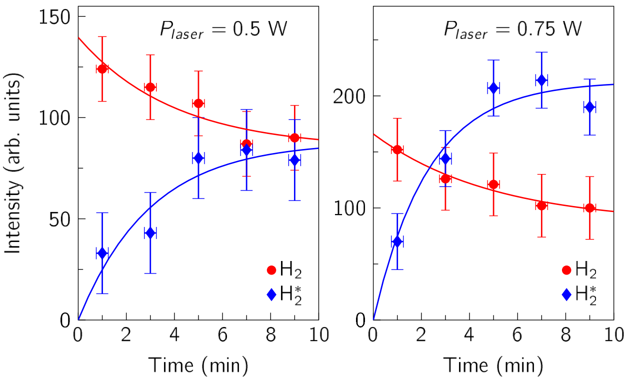

FIG. 3. Integrated intensities of the Raman signals due to H_2 (red) and H_2^* (blue) as a function of measurement time. Left: excitation laser power 0.5 W; right: 0.75 W. Nominal temperature: 4.5 K. Solid lines are guides for the eye.

were repeated at 110 ± 5 K as determined from the Stokes to anti-Stokes ratio of the Γ-phonon line.

Figure 4 shows the results obtained for 0.5 and 1 W. Clearly, the excitation light remains the decisive factor for the H_2-to-H_2^* transformation if the temperature is kept constant. The difference between nominal 4.5 K and 110 K is a *nonmonotonic* behavior of the H_2^* signal under excitation with 1 W. The 1838-cm^{-1} line reaches its maximal intensity within the first couple of minutes, but after that both hydrogen dimers disappear from the spectra with a characteristic time of a few minutes. Surprisingly, no other signals seem to appear in the Raman spectra at the expense of H_2 and H_2^*.

To understand these results we consider the following reactions:

$$H_2 + h\nu \longrightarrow H_2^*, \tag{1a}$$

$$H_2^* + h\nu \longrightarrow H_{bc}^+ + H_T^-, \tag{1b}$$

i.e., light-induced transformation of H_2 into H_2^* Eq. (1a) followed by dissociation of H_2^* into atomic hydrogen interstitials at elevated temperatures in Eq. (1b).

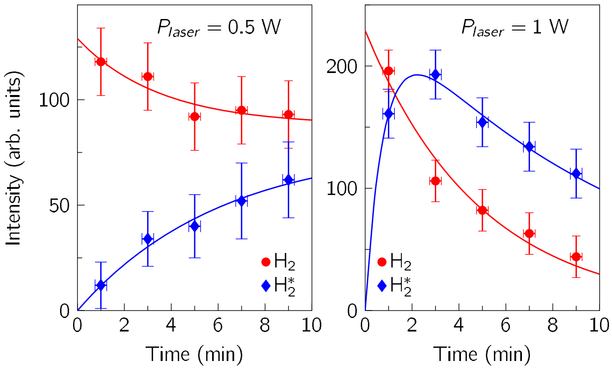

FIG. 4. Integrated intensities of the Raman signals due to H_2 (red) and H_2^* (blue) as a function of measurement time. Left: excitation laser power 0.5 W; right: 1 W. Temperature determined from the Stokes to anti-Stokes ratio of the Γ-phonon 110 ± 5 K. Solid lines are guides for the eye.

Isolated hydrogen in Si is a negative-U impurity, i.e., H^0 is higher in energy than H^+ and H^- with the transition $(+/-)$ level positioned 0.34 eV below the conduction band minimum [32,33]. Thus, in equilibrium, interstitial hydrogen occurs as H^+ in p-type and intrinsic Si and H^- in n-type Si.

In the positive charge state hydrogen is located at the bond-centered site (H_{bc}^+), whereas in the negative charge state it is at (or near) tetrahedral site (H_T^-). The calculated vibrational spectrum of H_{bc}^+ includes an asymmetric stretch, symmetric stretch, and a wag mode at 1994, 309, and 397 cm^{-1} [34]. The last two terms qualify as pseudolocal vibrational modes (see, e.g., [35]) since they occur within the phonon bath of Si. Such modes are sometimes seen as phonon replicas in photoluminescence (PL) spectra, but are inaccessible for IR absorption or Raman scattering due to their marginal sensitivity compared to that of PL.

The asymmetric stretch mode, on the other hand, matches very well the measured 1998 cm^{-1} [36]. This mode has an unusually large effective charge of $(3.0 \pm 0.3)e$ resulting in a very strong line in the IR absorption spectra. Unfortunately for the spectroscopic technique employed in this study, its selection rules are complementary to those of IR absorption, so that the 1998-cm^{-1} mode cannot be probed by the Raman scattering. Moreover, IR absorption cannot be employed to detect the products of fragmentation either since everything happens within a tiny excitation volume of about $20 \times 20 \times 0.4\ \mu\text{m}^3$.

Contrary to H_{bc}^+, the spectroscopic signatures of H_T^- are unknown. Calculations find two modes at 528 and 514 cm^{-1} [34], i.e., almost in resonance with the Γ-phonon of Si, which explains why isolated hydrogen at the tetrahedral site could escape an experimental observation this far.

Summing up the aforementioned, neither H_{bc}^+ nor H_T^- can be probed by the Raman scattering, which seems to be a reason why no concurrent changes in the spectra were detected while H_2 and H_2^* disappear under exposure to the excitation laser light. It has to be emphasized though that the reaction scheme given by Eq. (1) is one of several thinkable pathways. Since atomic hydrogen is “invisible” for the Raman scattering, the right side of Eq. (1b) may, in principle, represent all possible combinations of H_{bc} and/or H_T in different charge states.

If the same spot is remeasured after the sample was kept in the dark for the next few minutes, neither dimer recovers its original intensity. This can be accounted for by the low mobility of atomic hydrogen at the temperature of the experiment. The activation energy for diffusion of H_{bc}^+ has been measured to be 0.48 eV [37,38], which agrees with theoretical calculations [34,39]. The diffusion barrier of H_T^- has not been determined experimentally. Calculations come up with the value of 0.39 eV [34] implying that even for such a low barrier it would take at least days until hydrogen ends up in the next interstitial site at 110 K.

Another result worth mentioning is a similar behavior of ortho- and para-H_2 (see Figs. 1 and 2). The two types of hydrogen have distinctly different low-energy excitation states due to different sets of allowed rotational quantum numbers: odd for ortho- and even for para-H_2 [21]. Since the apparent photodissociation rate of both species is the same, its mechanism cannot be related to the rotational degrees of freedom. On the other hand, the relative stability of D_2 compared to H_2

implies that the masses of nuclei, the molecule consists of, should also be taken into account (see Fig. 1).

The H_2 and H_2^* dimers in Si and Ge were studied by *ab initio* theory in Refs. [30,40–42]. All calculations agree that the two dimers are essentially equally stable, whereby the interstitial molecule in Si is more favorable by, depending on the details of calculations, 0.1 to 0.2 eV. It is, therefore, not surprising that H_2 can be transformed into H_2^*. Yet, it is not clear what mechanism(s) is(are) responsible for this transformation and the subsequent photodissociation of H_2^*.

There are two basic types of photodissociation of a chemically bound molecule. The simplest one is a process in which a molecule either directly absorbs a photon into a repulsive excited electronic state or the photon excites first a binding electronic state which by itself cannot break apart. However, if the molecule subsequently undergoes a transition from the binding state to another electronic state whose potential is repulsive, the complex will ultimately decay. In the case of free H_2, its ionization energy (15.43 eV [24]) is well above that of the photons employed in our study (2.33 eV). On the other hand, the excited electronic states of the interstitial molecule are unknown. Because of this, we cannot, at least at the current stage, completely rule out this explanation of our results.

Since the energy of photons is seemingly too low to facilitate the direct photodissociation, absorption of multiple quanta could provide a necessary energy to overcome the fragmentation barrier [43–46]. However, the excitation power densities required for such a scenario are many orders of magnitude above those employed in our study that practically excludes the multiphoton dissociation as a mechanism responsible for the fragmentation of interstitial H_2.

Hydrogen-induced platelets may provide an insight into solution of this dilemma. These are two-dimensional structures where each Si–Si bond located in a (111) plane is replaced by two Si–H bonds with molecular hydrogen filling up the space between the hydrogenated Si layers [25,26]. Intermolecular interaction as well as interaction between the molecules and the lattice is rather weak, which is reflected in the frequencies of its vibrational modes at 4150 cm^{-1}, i.e.. close to those of free H_2. Notably, at temperatures below 100 K the hydrogen “gas” undergoes a phase transition forming a two dimensional “crystal” [47]. By contrast with interstitial H_2, Raman measurements performed on platelets do not reveal any change in the spectroscopic signatures of molecular hydrogen in the course of time. This implies that the photodissociation rate depends on particular location of the molecule in the Si lattice. In other words, the knowledge of excited states for the full system (H_2 embedded into the Si lattice) is necessary to solve the puzzle of the H_2 photodissociation [48,49].

Finally, we mention a possibility that the large concentrations of free carriers, i.e., electron-hole plasma, generated by the excitation light may also contribute to the dissociation of H_2. It is, however, not clear why this mechanism should work only for interstitial species leaving all other hydrogen-related defects intact.

IV. SUMMARY

In summary, photodissociation of interstitial H_2 and D_2 in single-crystalline Si in a laser field at 532 nm and a power density around 2×10^6 W/cm^2 was observed in the course of Raman scattering measurements. At temperatures below 100 K the molecule underwent a transition into a metastable H_2^* (D_2^*) state consisting of two Si–H (Si–D) units aligned along the $\langle 111 \rangle$ direction. At temperatures above 100 K both dimers dissociated, whereby the products of fragmentation were suggested to be atomic interstitials. Further experiments, i.e., Raman scattering with excitation lasers of different wavelengths, combined with first-principles theory are necessary to disclose the unsolved problems of interstitial H_2 in Si as well as other semiconductors, e.g., Ge and GaAs [50,51].

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