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Nonlinear optical study of the Si(111)7×7 to 1×1 phase transition: Superheating and the nature of the 1×1 phase

U. Höfer
Max-Planck-Institut für Quantenoptik, D-85740 Garching, Germany

Leping Li, G. A. Ratzlaff, and T. F. Heinz
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598-0218

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The reversible 7×7 $\leftrightarrow$ 1×1 phase transition of Si(111) is investigated by means of optical second-harmonic (SH) generation. The SH response increases sharply at $T_c \simeq 1130$ K. The symmetry and magnitude of the SH signal are compatible with an adatom gas model for the 1×1 phase in which the number of dangling bonds is increased by roughly 25% with respect to the 7×7 structure. The behavior observed under conditions of laser heating provides clear evidence of superheating of the Si(111)7×7 phase by more than 50 K above T_c on the nanosecond time scale.

I. INTRODUCTION

The reversible transition of Si(111)7×7 to a disordered 1×1 phase at $T_c \sim 1100$ K was first reported by Lander[1] in 1964 and has since been investigated extensively. In low-energy electron diffraction[1–3] (LEED) and reflection high-energy electron diffraction[4,5] (RHEED) measurements, the 7×7 superlattice spots disappear continuously over a temperature range of ~ 50 K. This observation has led to a discussion of whether the phase transition is second order, in violation of the Landau symmetry rules.[6] Spatially resolved measurements with reflection electron microscopy,[7] LEED microscopy,[8] and high-temperature scanning tunneling microscopy[9] (STM) have, however, revealed phase coexistence between the 7×7 and 1×1 domains at T_c, characteristic of a first-order transition. Further, in several studies it was shown that the (upper) step edges act as nucleation centers for the 7×7 phase.[7,10] Despite this recent progress, the kinetics of the phase transition as well as the mechanism leading to the instability of the 7×7 phase are still relatively poorly understood. This situation reflects, in part, the limited structural information available for the high-temperature 1×1 phase.

In the present work, we investigate the Si(111)7×7 $\leftrightarrow$ 1×1 phase transition with optical second-harmonic generation (SHG). It has been observed by us[11] and independently by Suzuki and Hirabayashi[12] that the second-order nonlinear optical response of Si(111) as a function of surface temperature increases abruptly at the critical temperature T_c. The distinct SH signature of the two surface structures allows us to study the effect of nanosecond heating pulses on the phase transition. In this paper, we show that it is possible to superheat the 7×7 phase by more than 50 K above T_c for a time of nanoseconds. The possibility of significant superheating is indicative of a first-order phase transition. In addition, we exploit the symmetry properties of SHG and its sensitivity to the Si dangling bonds to deduce information on the nature of the 1×1 phase. Our results provide direct evidence that this high-temperature phase is not fully disordered, but retains long-range C_{3v} symmetry. Within a simple model for the SHG response, we are able to deduce that the number of dangling bonds in the 1×1 phase is roughly 25% higher than that of the dimer-adatom-stacking-fault (DAS) model of the 7×7 phase.[13] The data agree with an adatom gas model[14] for the 1×1 phase, where 0.25 ML of adatoms preferentially occupy the T_4 sites of the bulk-terminated (111) surface.

II. EXPERIMENTAL

The experiments were performed in ultrahigh-vacuum chamber ($p < 2\times10^{-10}$ mbar) equipped with capabilities for LEED and Auger electron spectroscopy. The Si(111) samples, n-type with a resistivity of 10 Ω cm and a miscut of $< 0.25°$, were mounted on a liquid-nitrogen-cooled holder and cleaned *in situ* by removing the oxide layer at 1300 K. The sample temperatuare was controlled by passing a variable dc current through the wafer. Measurement of the sample temperature was obtained from a thermocouple cemented to the back of the Si wafer; for high sample temperatures, an infrared pryrometer was also employed. The overall accuracy of our temperature measurement is estimated to be ±15 K at 1100 K. The pump radiation for the SH measurements was provided by a Q-switched Nd:YAG (where YAG denotes yttrium aluminum garnet) laser operating at a wavelength of 1064 nm with a pulse duration of 10 ns and a repetition rate of 20 Hz. The unfocused laser beam with an approximately Gaussian profile of 5 mm diam was incident at 40° with respect to the surface normal. The plane of incidence was normal to the $[2\bar{1}\bar{1}]$ direction of the Si sample. For some measurements, the beam was apetured down to 2 mm in order to achieve a relatively uniform temperature profile over the illuminated area of the sample. The fluence of the incident radiation was varied between 15 and 100 mJ/cm^2.

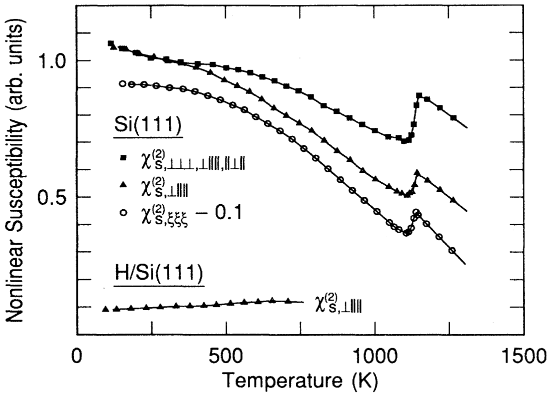

FIG. 1. Temperature dependence of the second-order nonlinear susceptibility $\chi_s^{(2)}$ of clean and hydrogen terminated Si(111) surfaces. The different tensor components are scaled relative to their values for clean Si(111) at $T_s = 300\,\mathrm{K}$.

III. RESULTS AND DISCUSSION

Before discussing the experimental results we briefly summarize the relevant symmetry properties of the SHG process.[16] The surface nonlinear susceptibility tensor $\chi_s^{(2)}$ for SHG is defined by the relation $\mathbf{P}_s(2\omega) = \chi_s^{(2)}: \mathbf{E}(\omega)\mathbf{E}(\omega)$ between the pump electric field and the surface nonlinear polarization. For the case of the Si(111)7×7 surface where C_{3v} symmetry prevails, the third-rank tensor $\chi_s^{(2)}$ consists of four different independent elements. The so-called isotropic components $\chi^{(2)}_{s,\|\perp\|}$, $\chi^{(2)}_{s,\perp\|\|}$, and $\chi^{(2)}_{s,\perp\perp\perp}$ arise from the symmetry breaking perpendicular to the surface. The corresponding SH signal is independent of the azimuthal orientation of the sample. The anisotropic component $\chi^{(2)}_{s,\xi\xi\xi}$ describes a nonlinear response arising with both the exciting field $\mathbf{E}(\omega)$ and induced polarization $\mathbf{P}_s(2\omega)$ in the surface plane. It arises because Si(111) lacks inversion symmetry with respect to a plane perpendicular to the $\xi = [2\bar{1}\,\bar{1}]$ direction.

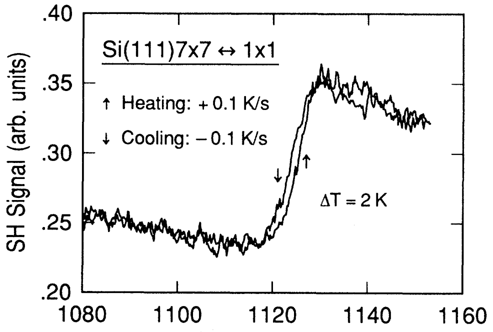

FIG. 2. SH signal from the anisotropic component $\chi^{(2)}_{s,\xi\xi\xi}$ of Si(111) for slow heating and cooling through the 7×7 ↔ 1×1 phase transition.

A. Quasistatic SH response

Figure 1 gives an overview of the measured temperature dependence of the SH response of Si(111). Both the isotropic ($\chi^{(2)}_{s,\|\perp\|}$, $\chi^{(2)}_{s,\perp\|\|}$, $\chi^{(2)}_{s,\perp\perp\perp}$) and the anisotropic ($\chi^{(2)}_{s,\xi\xi\xi}$) SH response of the clean surface exhibit an overall decrease with surface temperature interrupted by a sharp rise at the temperature $T_c \simeq 1130\,\mathrm{K}$. A comparison with $\chi_s^{(2)}$ of a hydrogen-terminated Si(111) surface reveals that the measured SH response of the clean surface originates from the top Si atoms and that bulk contributions to SHG may be neglected. The observed decrease of $\chi_s^{(2)}$ with increasing temperature may arise from changes in the thermal occupation of the narrow metallic surface states of Si(111)7×7,[17] as well as from temperature-dependent shifts in the energies of the surface electronic states. Irrespective of the origin of the overall temperature dependence, we may clearly associate the jump in the SH response observed at T_c with the transformation of the 7×7 reconstruction into the 1×1 phase.

More detailed data obtained for the anisotropic SH response in the vicinity of the phase transition are displayed in Fig. 2. In these measurements, the sample was cooled at a rate of 0.1 K/s from 1160 K to 1080 K and subsequently heated at the same rate. The jump in the SH response at the phase transition shows a hysteresis of $< 2\,\mathrm{K}$ between heating and cooling. This small hysteresis agrees with the result of a similar experiment by Suzuki and Hirabayashi,[12] but is less than the 5 K reported recently by Hasegawa *et al.*[5] for RHEED measurements. At the phase transition, the anisotropic SH intensity increases by a factor of 1.6, corresponding to a change of $\sqrt{1.6} = 1.27$ in $\chi^{(2)}_{s,\xi\xi\xi}$. The magnitude of the jump is very similar for the isotropic $\chi^{(2)}_{s,\perp\|\|}$ component. It is slightly higher ($\sqrt{1.9}$) for the mixture of isotropic components measured for *p*-polarized input and output radiation.

The observed signal changes at the phase transition impose some important constraints on possible models for the Si(111)1×1 phase. In particular, the presence of the anisotropic element $\chi^{(2)}_{s,\xi\xi\xi}$ for the 1×1 phase excludes the possibility of a totally disordered 1×1 phase, since such a surface would exhibit isotropic ($C_{\infty v}$) symmetry macroscopically and would not permit a finite value for $\chi^{(2)}_{s,\xi\xi\xi}$.[16] Indeed, earlier experimental studies of the disordering of the 7×7 reconstructed surface by sputtering and low-temperature Si deposition have demonstrated how complete surface disordering causes the anisotropic SH response to vanish.[18] Our results thus exclude models of the Si(111)1×1 phase that involve molten surfaces[3] or disordered structures comprised of small randomly distributed domains with crystalline order.[19]

Based on the observation of diffuse electron diffraction patterns, it has been proposed that the high-temperature Si(111)1×1 surface consists of a gas of adatoms in threefold sites on the bulklike (111) surface.[14] Just as for the adatoms of the DAS model, these atoms tie up three dangling bonds (dbs) of the top layer and reduce the energy of the system. High-temperature STM data, in which atomic resolution suddenly vanishes at T_c,[9] also support

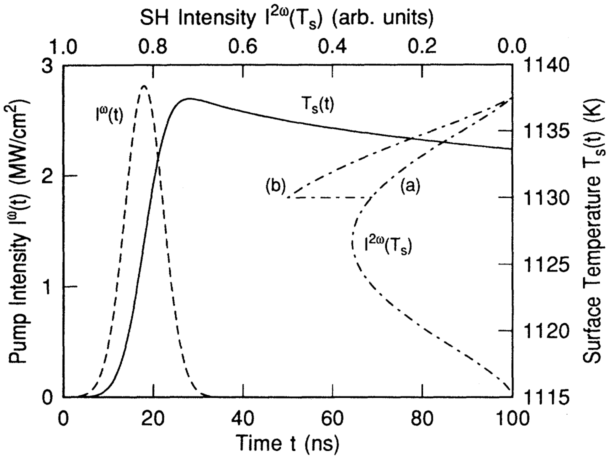

FIG. 3. Calculated surface temperature $T_s(t)$ of silicon due to heating by a laser pulse with intensity $I^{\omega}(t)$ and the calculated SH intensity $I^{2\omega}$ generated by the same pulse. $I^{2\omega}$ is plotted as a function of T_s in two cases: (a) $\chi_s^{(2)}$ is independent of T_s, (b) $\chi_s^{(2)}$ is a step function at $T_s = T_c$.

such a model with rapidly diffusing adatoms. As we shall see below, this type of model is compatible with the SHG data, from which we may indeed make some further inferences about the structure of the 1×1 phase.

Our discussion of the SHG data is based on the approximation that the nonlinear susceptibility is proportional to the number of dbs (adatoms + restatoms) on the surface. Such a relation was inferred from previous SHG experiments on hydrogen adsorption on the Si(111)7×7 surface.[15] We assume that the relationship also holds for the 7×7 ↔ 1×1 phase transition. The increase of $\chi^{(2)}_{s,\perp\|\|}$ by a factor of 1.27 at the phase transition then translates into 0.49 dbs per (111) surface atom for the 1×1 phase compared to 0.39 dbs for the 7×7 phase.[13] Since each adatom quenches three dbs and creates one new db, we arrive at an adatom coverage of $\theta_{\rm ad} = 0.26\,$ML for the Si(111)1×1 phase. Similarly, from the 1.38-fold increase of the mixture of all isotropic tensor elements, we derive $\theta_{\rm ad} = 0.23\,$ML. Both values are close to the adatom coverage of 0.245 ML for the DAS model of the 7×7 reconstruction. The increased number of dbs of the 1×1 phase is, therefore, seen to arise principally from the breakup of the dimers of the 7×7 units. The local arrangement of dbs is likely to be very similar for both phases, which in turn justifies the simplification of neglecting changes of the electronic structure at T_c inherent in our modeling. The inferred adatom coverage of $\theta_{\rm ad} = 0.23 - 0.26\,$ML for the Si(111)1×1 phase is similar to that of 0.20 − 0.22 ML observed by STM on rapidly quenched 1×1 surfaces.[20]

Up to this point, we have not differentiated between the two types of threefold coordinated sites that adatoms may occupy above the bulk-terminated Si(111) surface: the T_4 sites above second-layer Si atoms and the H_3 sites in the threefold hollow positions.[4] If we consider the anisotropic SH response, we see that adatoms in each of these sites will, within our dangling-bond model, make a contribution of equal magnitude but opposite sign to $\chi^{(2)}_{s,\xi\xi\xi}$. Thus the fact that the anisotropic SH response increases by an amount comparable to that of the isotropic response at the phase transition suggests that there is a strong preference for occupancy of one of the two sites. We would expect the favored location of the adatoms to be the T_4 sites, since this is the case for the adatoms in the 7×7 reconstruction. It may be noted that even at the elevated temperature T_c of the phase transition, a modest difference in binding energy of 0.1 eV is expected to produce substantial preferential occupancy of one site over the other.

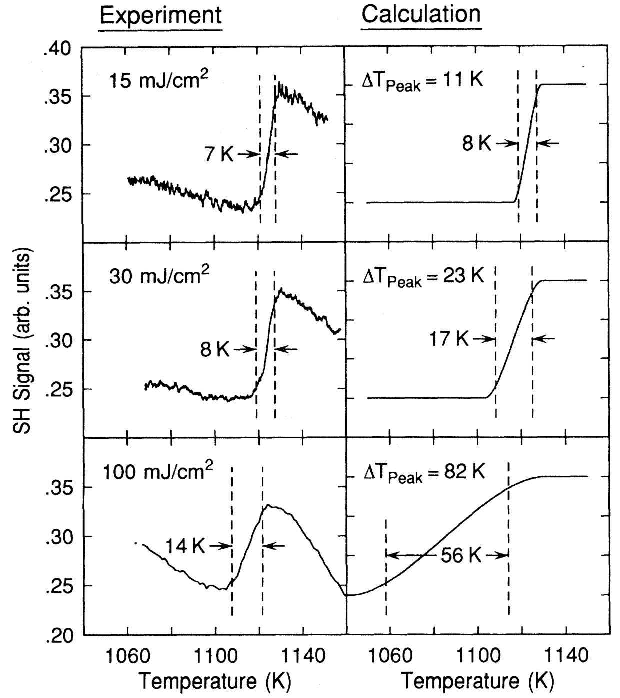

FIG. 4. Experimental SH response at the 7×7 ↔ 1×1 phase transition for three different laser fluences compared to calculation for a phase transition without superheating.

B. Transient SH response of the laser-heated sample

We now turn to the effect of laser-induced transient heating on the phase transition. The calculated transient temperature profile at the surface is shown in Fig. 3 for a laser fluence of $30\,{\rm mJ/cm^2}$ with an assumed Gaussian temporal profile and a duration of 10 ns. In the numerical calculation, heat diffusion normal to the surface is taken into account using temperature-dependent values for the heat capacity C_p, heat conductivity κ, and the absorption coefficient α of silicon.[21,22] As can be seen from Fig. 3, the surface temperature rises with the integrated energy deposition by the pump pulse and then decays by diffusion in a fraction of a μs. The monotonic rise of the surface temperature during the course of a laser pulse causes the SH response to sample an average temperature higher than the base temperature of the sample (Fig. 3). We may thus examine the behavior of the phase transition under conditions of rapid heating simply by performing SHG experiments over a range of pump fluences.

Figure 4 displays SH data for three different pump fluences. The experimental SH intensities are plotted in the left column for each pump fluence as the base temperature of the sample is swept (typically at a rate of 0.1 K/s) through the phase transition. We define the apparent width of the phase transition Δ by the temperature difference required for the SH signal to undergo 10% to 90% of its maximum change. In the right column of Fig. 4, we present calculations of the SH response on the assumption that the surface *instantaneously* reaches its equilibrium structure during the temperature transient. To capture the basic physics of the phase transition as simply as possible, we approximate the equilibrium SH response as a step function at the critical temperature T_c and omit the weaker temperature dependence in the 7×7 and 1×1 phases of the surface. We then obtain the SH response as a function of the base temperature of the sample from a numerical calculation over the pump-induced temperature transient. As the pump fluence is increased, the transient temperature rise grows and the temperature of the phase transition T_c is reached at reduced base temperatures of the sample. Thus, if the response of the surface to the temperature transient is indeed instantaneous, we expect to see the influence of the phase transition appear at lower and lower base temperatures as the pump fluence is increased. By the same token, the apparent width Δ of the phase transition will increase with increasing pump fluence. These features can be seen in the right column of Fig. 4.

A comparison between the left and right columns of Fig. 4 reveals that the experimental widths Δ increase only weakly with increasing pump fluence, while the widths calculated for an instantaneous phase transition grow significantly. Obviously a substantial fraction of the 7×7 phase must persist at temperatures $T > T_c$ for the duration of the 10-ns laser pulse. The superheating effect is already visible at a fluence of 30 mJ/cm^2: the calculated width is 17 K, while the measured width is only 8 K, comparable to that of 7 K observed at a fluence of 15 mJ/cm^2. The effect is more pronounced for the highest pump fluence of 100 mJ/cm^2. If the surface structure followed the temperature profile instantaneously, the transition would be smeared out over $\Delta = 56\,\mathrm{K}$. In fact, the experimental width increases only to $\Delta = 14\,\mathrm{K}$. The main uncertainty in determining the degree of superheating in our analysis is associated with the value of the attenuation coefficient α of the pump radiation on the heated silicon sample.[22] Since no direct experimental measurements are available for the relevant temperature range, we have relied on theoretical data known to underestimate α substantially.[22] It follows that our calculated temperature transients understate the actual temperature rise and that the calculated widths in Fig. 4 should be regarded as lower bounds. The observed superheating certainly exceeds 50 K; it probably exceeds 100 K.

Since superheating is expected only for phase transitions with latent heat,[6] our findings provide clear evidence for the first-order character of the 7×7 ↔ 1×1 phase transition. It is instructive to compare our result of substantial superheating with the behavior observed by others for surface and bulk melting. In the case of surface melting, superheating has been observed on a time scale of a few hundred picoseconds.[23] In general, however, it is difficult to achieve substantial superheating, because real surfaces have many defects that may act as nucleation centers for the melting process. For bulk Si(111), laser-induced disordering has been found to occur as fast as 100 fs.[24] This comparison implies that the 7×7 ↔ 1×1 phase transition differs significantly from surface melting, as we concluded earlier based on the large anisotropic SH response of the 1×1 phase.

At first glance, superheating on a nanosecond time scale does not seem to be surprising within a model of the 1×1 phase that involves additional adatoms. With diffusivities on the order of $10^{-8}\,\mathrm{cm}^2/\mathrm{s}$, it takes milliseconds for Si atoms to diffuse across terraces of, say, 200 Å width. A breakup of the dimers of the 7×7 structure should, however, require only a few picoseconds. If this were indeed the initial stage of the phase transition, we would then expect to observe a rapid increase in the SH response from the creation of additional dbs, followed by a slower decrease as these new dbs were quenched by adatoms diffusing from the steps. The fact that the 7×7 surface persists at temperatures well above T_c for a period of nanoseconds, therefore, suggests that the driving force for the 7×7 to 1×1 phase transition is the instability of the step edges, which provide the nucleation center for the phase transition. Only as the adatoms diffuse over the surface is the 7×7 unit cell dissolved and the bulk-terminated structure formed.

IV. CONCLUSION

In summary, we have examined the nature of the Si(111)7×7 ↔ 1×1 phase transition by optical SHG. From the symmetry properties of the SH signal in the 1×1 phase, we are able to preclude models in which the surface layer is fully disordered. The magnitude of the SH signals can be understood on the basis of a model of the 1×1 surface in which the bulk-terminated surface is decorated with adatoms, provided that the density of adatoms is ~ 0.25 ML and that they preferentially occupy one of the two distinct threefold sites. By examination of the SH response for differing laser fluences, we were able to establish that the Si(111)7×7 surface was stable under significant superheating for a period of nanoseconds. Such superheating implies that the phase transition has first-order character and further suggests that the transformation from the 7×7 reconstruction to the 1×1 phase is driven by diffusion of adatoms from the steps, rather than by a spontaneous dissolution of the 7×7 unit cell.

After completion of this work, Suzuki *et al.*[25] published the results of a pump-probe experiment of the Si(111)7×7 to 1 × 1 phase transition with delay times ≥ 20 ns between the heating pulses and the SHG probe pulses. No indication of the 7×7 reconstructed surface undergoing a transition to the 1×1 phase during the duration of the transient surface heating of $\simeq 1\,\mu\mathrm{s}$ was observed.[25] These results are thus in agreement with the evidence of a substantial superheating of the Si(111)7×7 phase provided in the present paper and extend it to the microsecond time scale.

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