Time-resolved reflection high-energy electron diffraction study of the Ge(111)-$c(2\times8)-(1\times1)$ phase transition

Xinglin Zeng, Bo Lin, Ibrahim El-Kholy, and Hani E. Elsayed-Ali*

Department of Electrical and Computer Engineering, Old Dominion University, Norfolk, Virginia 23529

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The dynamics of the Ge(111)-$c(2\times8)-(1\times1)$ phase transition is investigated by 100-ps time-resolved reflection high-energy electron diffraction. A laser pulse heats the surface while a synchronized electron pulse is used to obtain the surface diffraction pattern. Slow heating shows that the adatoms in Ge(111)-$c(2\times8)$ start to disorder at ~510 K and are converted to a disordered adatom arrangement at 573 K. For heating with 100-ps laser pulses, the Ge(111)-$c(2\times8)$ reconstructed adatom arrangement starts to disorder at 584 ± 16 K, well above the onset temperature of ~510 K for the disordering of Ge(111)-$c(2\times8)$ observed for slow heating. [S0163-1829(99)06523-6]

At room temperature, the clean unstrained Ge(111) surface displays a stable centered (2×8) reconstructed structure.[1–3] The $c(2\times8)$ reconstruction is described by a quarter monolayer of adatoms bonded on T_4 sites of a bulk-terminated Ge(111). Scanning tunneling microscopy (STM) studies show $c(2\times8)$ domains oriented along the three different but equivalent directions at the surface, with domain size ranging from 200 to 2000 Å depending on the surface preparation.[4,5] The boundaries between these domains are accommodated by the formation of local (2×2) adatom structures.[6] Near 573 K, the surface undergoes a reversible phase transition in which the $c(2\times8)$ structure starts to disorder from the domain boundaries.[4] As temperature is increased, the disordered regions grow in size, and at ~573 K the whole adatom layer is totally converted into an apparent (1×1) phase as indicated by low-energy electron diffraction (LEED).[3] Measurements of the Ge $3d$ core level show that the Ge(111)-$c(2\times8)-(1\times1)$ phase transition is of the order-disorder type.[7,8] There are other techniques that have been applied to study the $c(2\times8)-(1\times1)$ phase transition such as electron energy loss spectroscopy,[9] core level study,[7,8] medium-energy ion scattering,[10,11] spectroscopic ellipsometry,[12] helium atom scattering,[13] and photoelectron diffraction.[14] However, none of these techniques gave information on the temporal dynamics of this phase transition. Molecular dynamics (MD) simulations provide a microscopic description of the dynamics of the atomic system,[15] however, direct experimental evidence has not been available.

We use time-resolved reflection high-energy electron diffraction (RHEED) to investigate the evolution of the phase transition. The Ge(111)-$c(2\times8)$ adatom layer starts to disorder at 584 ± 16 K by 100-ps laser pulse heating, whereas for slow heating it starts to disorder at ~510 K. The phase transition is observed to be reversible.

Time-resolved RHEED was described in detail elsewhere.[16] This technique was used to probe surface melting and superheating of lead and bismuth.[17–21] The fundamental of a Nd:YAG laser (YAG denotes yttrium aluminum garnet) [$\lambda=1.06\,\mu$m, full width at half maximum (FWHM) = 100 ps] is split into two beams. The first interacts with the sample surface at near normal incidence, providing a laser pulse heating source with a beam diameter of ~9 mm measured at FWHM. The second is frequency quadrupled to the ultraviolet ($\lambda=0.266\,\mu$m) and is incident on the cathode of a photoactivated electron gun, producing an electron pulse synchronized with the laser and with a temporal width comparable to that of the laser pulse. The resulting electron beam is incident on the surface of the sample in a glancing angle probing the first few atomic layers. The diffracted electrons are amplified by microchannel plate proximity focused to a phosphor screen. The resulting RHEED pattern is lens imaged onto a charge coupled device camera for quantitative intensity analysis. The energy of the electrons is 21 keV. The pulse-to-pulse heating laser fluctuation is within $\pm10\%$. The spatial nonuniformity of the beam across the sample is measured to be $\pm12\%$. An optical delay line sets the time between the heating laser pulse and the probing electron pulse. This allows RHEED patterns to be monitored throughout the laser pulse heating process. The laser is operated at 50-Hz repetition rate. A total of 3000–5000 laser pulses were used to acquire each datum. Pump-probe LEED with ~10-ns temporal resolution was previously conducted on Ge(111) to study the melting phase transformation. Because of detector size limitations, only a single reflection was monitored. Results were consistent with loss of surface crystal order during laser annealing.[22] Here, we study the Ge(111)-$c(2\times8)-(1\times1)$ reconstruction phase transition with 100-ps time-resolved RHEED.

The Ge(111) single crystal was cut to 6×5 mm^2 from a 340-μm-thick wafer n doped with antimony with a resistivity of 1.4–2.2 Ω cm. The surface has a vicinal angle of $\pm0.5°$ off (111), and was polished to be epitaxy ready. The sample was heated by passing direct current through it. The temperature was monitored by a thermocouple pressed against the surface of the sample with ±2 K uncertainty. The surface was prepared by cycles of Ar$^+$ bombarding at room temperature (500 eV, at normal incidence) followed by annealing at 700 °C for 20 min. The surface was then found to be clean as determined with Auger electron spectroscopy. The $c(2\times8)$ structure was clearly observed with RHEED at room temperature. The experiments were performed in an ultrahigh vacuum chamber with a base pressure in the low 10^{-10} torr.
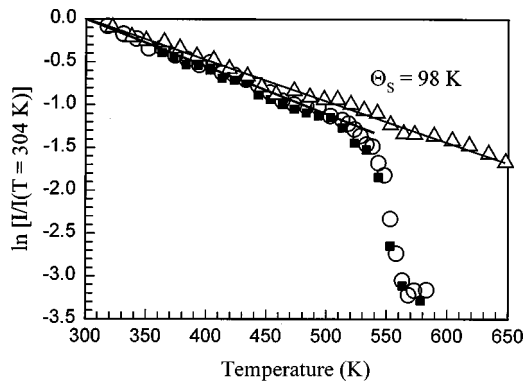
FIG. 1. Normalized RHEED intensities, $I/I(T=304\text{ K})$, of the $(0\frac{1}{2})$ and (01) diffraction streaks versus temperature are plotted on a semilogarithmic scale. The (01) streak ($\triangle$) shows the Debye-Waller behavior over 300 K to 650 K, with an effective surface Debye temperature $\Theta_s=98\text{ K}$. The $(0\frac{1}{2})$ streak ($\blacksquare$, with temperature decrease; $\bigcirc$, with temperature increase) shows the reversible Ge(111)-$c(2\times8)$–(1×1) phase transition.

Measurements of the RHEED streak intensity were performed as a function of the surface temperature. An UV lamp was used to excite the cathode of the photoactivated electron gun to produce a continuous electron beam. The electron beam was incident along the $\langle1\bar{1}0\rangle$ azimuth at an angle of $\sim2.7°$ from the surface, resulting in a probed depth of ~4.2 Å, corresponding to ~1.3 bilayers of Ge(111). The $(0\frac{1}{2})$ and (01) streaks were examined at the same time. RHEED streak intensities normalized to that at 304 K versus surface temperature are shown in Fig. 1. The exponential Debye-Waller behavior of the $(0\frac{1}{2})$ streak is observed below ~510 K. At higher temperatures, deviation from the exponential behavior occurs, indicating the onset of adatom disorder in the $c(2\times8)$ structure. The coexistence of disordered and ordered regions on the surface at temperatures well below the 573-K transition temperature was previously observed by STM.[4] Our results agree with the STM observations. The Debye-Waller behavior of the (01) streak persists above 573 K. The Debye-Waller factor is used to extract the transient temperature on the surface during laser pulse heating, since it is not affected by the Ge(111)-$c(2\times8)$–(1×1) phase transition. The MD simulation of Takeuchi, Selloni, and Tosatti showed that the mean square displacements are larger for outer atoms in the first bilayer and decrease for the deeper atoms.[23] The effective surface Debye temperature for the Ge(111) surface was calculated to be $\Theta_s=98\text{ K}$ from the Debye-Waller factor of the (01) streak,[24] whereas the Ge bulk Debye temperature Θ is 370 K. This is in agreement with results obtained from photoelectron diffraction and LEED.[14,25]

In order to determine the laser-pulse-induced temperature rise on the Ge(111) surface, time-resolved RHEED intensities of the (01) streak normalized to that at the base temperature of 442 K were obtained for different delay times between the heating laser pulse and the probing electron pulse. Results are shown in the inset of Fig. 2. The transient temperature rise was obtained using the Debye-Waller factor of the (01) streak from Fig. 1. The transient temperature evolution of the Ge(111) surface is given in Fig. 2, where the solid line represents the prediction from a one-dimensional heat
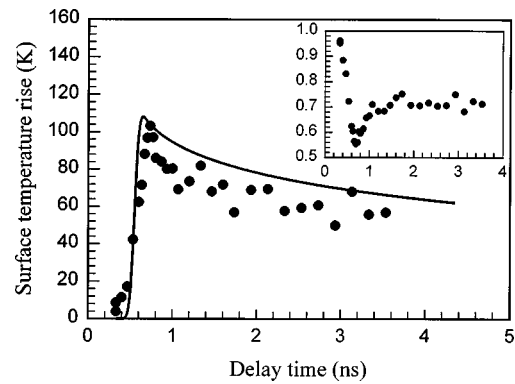

FIG. 2. Transient temperature rise on the Ge(111) surface during laser pulse heating with a peak fluence of $1.8\times10^8\text{ W/cm}^2$ and the surface maintained at a base temperature of 442 K. The experimental results ($\bullet$) were obtained from the (01) streak using the Debye-Waller factor of the (01) streak in Fig. 1. The solid line is the prediction of a one-dimensional heat diffusion model. The inset shows the corresponding normalized RHEED streak intensity $I/I(T=442\text{ K})$ versus delay time.

diffusion model.[26] The parameters used in this model are heat capacity equal to $1.844\times10^6\text{ J m}^{-3}\text{ K}^{-1}$,[27] thermal conductivity equal to $39.8\text{ W m}^{-1}\text{ K}^{-1}$,[27] reflectivity equal to 0.379,[28] absorption coefficient equal to $1.8\times10^6\text{ m}^{-1}$,[29] and a 100-ps FWHM Gaussian laser pulse with peak fluence equal to $1.8\times10^8\text{ W/cm}^2$. The experimental results agree well with the heat diffusion model. Figure 2 also relates the maximum transient temperature rise on the Ge(111) surface to the peak fluence of the heating laser pulse. This is used to determine the maximum surface temperature rise which is proportional to the laser peak fluence.

We next raised the sample temperature close to the onset temperature of the reconstruction phase transition and used a fixed laser fluence to further raise this surface temperature in a transient manner. The time-resolved RHEED intensity was monitored by fixing the delay time at the time at which the RHEED intensity is minimum, which is temporally close to the time of maximum surface temperature rise. RHEED streak intensity of the $(0\frac{1}{2})$ streak normalized to that at the base temperature was obtained for various peak laser fluences. Results are shown in Fig. 3 for three pump-probe scans representing base temperatures successively closer to 510 K. In each of these scans, the exponential behavior with temperature remains for lower laser peak fluences with a corresponding surface Debye temperature Θ_s of 110, 109, and 87 K for base temperatures of 442, 473, and 507 K, respectively. This is within $\pm12\%$ of $\Theta_s=98\text{ K}$ observed for the slow heating. Deviation from exponential behavior occurs at higher peak laser fluences depending on the base temperature, indicating that the adatoms are no longer bonded to the T_4 sites by a harmonic oscillator and start to diffuse as the temperature is increased. From Fig. 1, we see that this starts at ~510 K, which is well below the thermodynamic transition temperature of 573 K. This behavior was explained as premelting,[4] or as a result of surface strain.[12] A MD simulation showed that the energy barrier for the adatom diffusion is decreased when surface vacancies are present.[30] It is reasonable to expect that adatom diffusion starts at a lower temperature than the thermodynamic transition temperature, because surface vacancies are always present on a
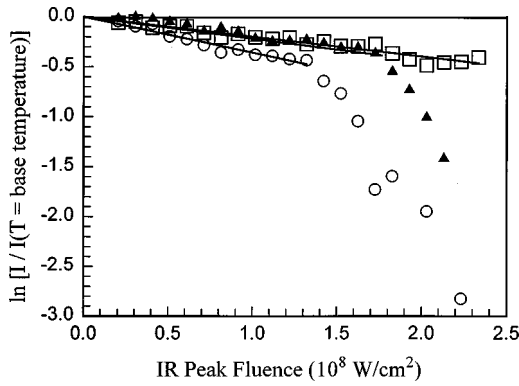
FIG. 3. Time-resolved RHEED intensities of the $(0\frac{1}{2})$ streak normalized to those at base temperature ($\bigcirc$, 507 K; $\blacktriangle$, 473 K; $\square$, 442 K) versus laser peak fluences are plotted on a semilogarithmic scale. RHEED intensities are obtained at a time near which the surface temperature is maximum. The maximum temperature rise on the Ge(111) surface is ~110 K for a laser peak fluence of 1.8 $\times 10^8$ W/cm^2. Deviations from Debye-Waller behavior occur at higher temperatures compared to that in Fig. 1 for slow heating.

real Ge(111) surface. STM observations showed that the disorder starts from the domain boundaries where surface vacancies are present.[4]

In Fig. 3, the deviations from exponential Debye-Waller behavior occur at laser peak fluences of 13.4 ± 1.6 $\times 10^7$ W/cm^2 for a base temperature of 507 K, and 17.3 $\pm 2.1\times 10^7$ W/cm^2 for a base temperature of 473 K. The indicated errors are due to nonuniformity of the laser beam across the probed sample area. These two fluences correspond to maximum transient temperature rises of 82 ± 10 and 106 ± 13 K, respectively. Therefore, for 100-ps laser heating, the Debye-Waller behavior of the $c(2\times8)$ lattice remains up to 589 ± 10 and 579 ± 13 K for the two curves showing reconstruction in Fig. 3, giving an average of 584 ± 16 K. For slow heating, the $c(2\times8)$ lattice starts to disorder at ~510 K. For both slow heating and 100-ps laser heating, the Ge(111)-$c(2\times8)$–(1×1) phase transition occurs over a temperature range ΔT, which we define as the interval between the onset temperature of the phase transition and the temperature at which the RHEED intensity is 10% of that at the onset temperature. The onset temperature of the phase transition is that when the RHEED intensity deviates from the Debye-Waller behavior. For 100-ps laser heating, Fig. 3, the Ge(111)-$c(2\times8)$–(1×1) phase transition starts at 584 ±16 K and spreads over a temperature range ΔT of 58 K, whereas for slow heating, Fig. 1, the phase transition starts at 510 K and spreads over a temperature range of 55 K. Therefore, we conclude that the $c(2\times8)$ structure is overheated by 74 ± 16 K above the onset temperature of adatom disordering observed under thermodynamic equilibrium conditions of slow heating. MD simulations showed that the Ge(111)-$c(2\times8)$ structure survives for 3 ps at 1200 K,[31] whereas our experimental results show that the $c(2\times8)$ lattice persists up to 584 ± 16 K for 100-ps laser pulse heating. However, the MD simulation assumes an ideal step heating which brings the surface to high temperature instantaneously and keeps it at that temperature thereafter; while in our experiment, the sample is heated to a high temperature in a time comparable to the laser pulse width and the temperature
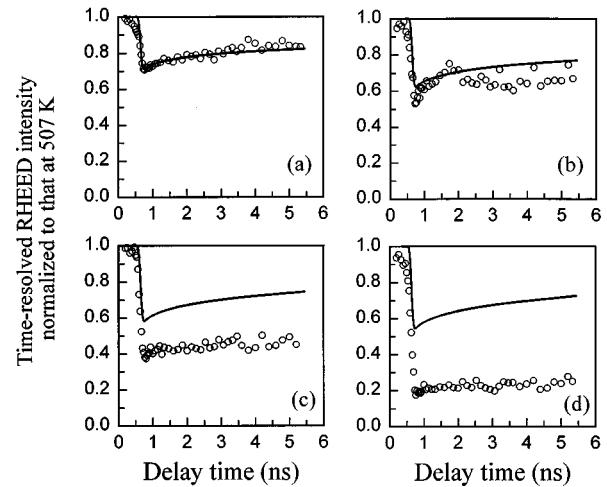

FIG. 4. Time-resolved normalized RHEED intensity of the $(0\frac{1}{2})$ streak of the Ge(111)-$c(2\times8)$ surface subjected to varying laser peak fluences (I_p). The solid line is from a one-dimensional heat diffusion model, and converting the temperature rise to RHEED intensity of the $(0\frac{1}{2})$ streak using the Debye-Waller factor of that order. The surface is kept at a base temperature of 507 K. (a) $I_p = 10.2\pm1.2\times 10^7$ W/cm^2, consistent with that expected from heat diffusion. (b) $I_p = 14.2\pm1.7\times 10^7$ W/cm^2 and (c) $I_p = 16.3\pm2.0$ $\times 10^7$ W/cm^2 deviate from that expected from heat diffusion, indicating partial disordering of Ge(111)-$c(2\times8)$. (d) $I_p = 18.3\pm2.2$ $\times 10^7$ W/cm^2, near total conversion to Ge(111)-(1×1) structure.

decreases after that by heat diffusion to the bulk.

Further experiments were performed to examine the temporal behavior of the Ge(111)-$c(2\times8)$–(1×1) phase transition. The normalized RHEED $(0\frac{1}{2})$ streak intensities were obtained at various delay times between the arrival of the heating laser pulse and the electron probe pulse at the surface of the sample. Results for different incident laser peak fluences are shown in Fig. 4. The base temperature of the sample is 507 K. The solid line is from a one-dimensional heat diffusion model, converting the obtained temperature rise to normalized $(0\frac{1}{2})$ streak RHEED intensity using the Debye-Waller factor of that diffraction order obtained at temperatures below the phase transition. Deviation of the experimental data from the solid line is due to adatom disordering. In Fig. 4(a), the sample was heated to a maximum surface temperature of 569 ± 7 K when subjected to a laser peak fluence of $10.2\pm1.2\times 10^7$ W/cm^2. For this case, the Ge(111)-$c(2\times8)$ lattice is overheated in the Debye-Waller region without disordering. This set exhibits qualities consistent with laser heating and cooling as predicted from heat diffusion. In Figs. 4(b), 4(c), and 4(d), sufficient laser peak fluences were provided to heat the sample to maximum surface temperatures of 593 ± 10, 607 ± 12, and 619 ± 13 K, respectively, which are above the onset temperature of 584 K for the Ge(111)-$c(2\times8)$–(1×1) phase transition observed for 100-ps laser heating. For these sets, the $(0\frac{1}{2})$ streak intensity exhibits an initially fast decrease within ~200 ps. For the set (b), some limited Ge(111)-$c(2\times8)$ disordering is observed. For the sets (c) and (d), the disordering is clearly observed and is maintained for the duration of the probed time, which is ~4.5 ns from the time of the peak laser fluence on the surface. For the lower fluence of Fig. 4(c), the $c(2\times8)$ shows only partial disorder. The lack of complete

extinction of the $(0\frac{1}{2})$ RHEED intensity is thought to be due to the combination of the effects of the growth of the disorder from domain boundaries, and perhaps microscopic laser fluence variation at the surface beyond that measured by scanning the laser beam profile. The decrease in the surface temperature by heat diffusion results in a surface temperature of 559 ± 6 and 566 ± 7 K, respectively, for (c) and (d) at ~4.5 ns from the time of the peak laser fluence. For these temperatures the surface disorder persists. The Ge(111)-$c(2\times8)$ structure is observed, however, to fully recover before the next laser pulse for 50-Hz repetition rate. In all of the experiments reported here, no surface damage was observed.

In summary, we have investigated the dynamic behavior of the Ge(111)-$c(2\times8)$–(1×1) phase transition. For slow heating, our RHEED results show that the adatoms in the Ge(111)-$c(2\times8)$ reconstruction state start to disorder at ~510 K and are converted to a disordered adatom arrangement at ~573 K. This is consistent with previous LEED and STM observations.[3,4] However, by 100-ps laser pulse heating, time-resolved RHEED measurements show that the disorder starts at 584 ± 16 K, 74 ± 16 K above the onset temperature for the disordering under thermodynamic equilibrium. This result is in qualitative agreement with the overheating of Ge(111)-$c(2\times8)$ which was previously predicted from MD simulations.[31]

*Author to whom correspondence should be addressed. FAX: (757) 683-3220. Electronic address: elsayed-ali@ece.odu.edu

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