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Simultaneous layer-by-layer and step-flow sublimation on the CdTe(001) surface derived from a diffraction analysis

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High-resolution low-energy electron diffraction (HRLEED), mass spectrometry, and computer simulations using a solid-on-solid model were combined to study the sublimation kinetics of the CdTe(001) surface. The HRLEED spot profile measurements show that specular spot intensity oscillations during sublimation are caused by an only small variation ($\sim$15%) of the step density, and that the step flow contribution dominates the sublimation process. Consequently, two different activation energies were derived from the mass desorption (1.55 eV) and the oscillation frequency of the HRLEED intensity (1.94 eV). These findings are confirmed by computer simulations of the sublimation on irregularly stepped surfaces. These show a mixed sublimation mode with vacancy nucleation (leading to intensity oscillations) only on the largest terraces and step flow otherwise. On the basis of these results, we can explain discrepancies in earlier determined sublimation energies.

I. INTRODUCTION

The molecular-beam epitaxy (MBE) growth of high-quality binary and ternary compounds, such as CdTe and $Hg_xCd_{1-x}Te$, is of great technological interest. For optimizing and modeling[1,2] of the MBE growth of these materials, a detailed knowledge of the kinetic surface processes is of large importance. Especially, sublimation processes are rather easy to study and can provide detailed information on the kinetics of microscopic processes such as desorption or diffusion.[3–8] Therefore, in the past years the experimental determination of sublimation rates has been a subject of continuous interest in the research on MBE-grown semiconductor compound materials under both technological and basic physical aspects.[1,7,9–12]

In this paper, we report a detailed experimental investigation on the sublimation process on the CdTe(001) surface. This surface constitutes a common substrate for the MBE growth of low-band-gap materials.[13] For CdTe up to now two different approaches have been chosen to study sublimation: The desorption flux was measured by quadrupole mass spectrometry (QMS) of the desorption products[10] or by weight loss measurements.[11] Alternatively, the evolution of the surface roughness during the sublimation process was studied, for instance, by using reflection high-energy electron diffraction (RHEED).[1,7,9]

The derivation of sublimation rates from RHEED oscillations is usually based on the assumption that exactly one monolayer of CdTe, (i.e., one layer of Cd *and* Te atoms) is evaporated per oscillation period. This implies that there is no significant step flow contribution to the desorption flux, and that the oscillating part of the step density, which causes the RHEED oscillations, is large compared to the average total density of steps. Only in this case the RHEED oscillation frequency is actually proportional to the mass desorption flux. However, due to a non-ideal long scale surface morphology, which could result from, e.g., a small miscut during the substrate preparation and/or due to dislocation induced growth spirals,[14] a nonzero step density is usually unavoidable. As RHEED specular beam intensities are not sufficient to determine step densities quantitatively,[15,16] one has to be aware that a pure layer-by-layer sublimation mode cannot be derived from RHEED intensity oscillations alone. Therefore it is essentially unclear, whether the activation energies measured in RHEED really correspond to the sublimation energy of CdTe(001). Rather early performed measurements on alkali halide surfaces[4] and silicon[5] have already demonstrated that dominant polyvacancy nucleation (leading to a layer-by-layer desorption) occurs only on large terraces and for high-desorption fluxes, but that the desorption flux is generally dominated by step flow sublimation. Thus RHEED oscillation measurements are generally not sufficient for the determination of sublimation rates. We note that the analogous problem for MBE growth has been extensively studied using vicinal surfaces.[17,18]

In this context, it is interesting to note that the experimental results for the sublimation energy of CdTe(001) differ significantly. The frequencies of the RHEED intensity oscillations during sublimation show an Arrhenius behavior.[1,7,9] The activation energies determined in the temperature range from 300 °C to 400 °C agree well within small errors (1.89 eV–1.95 eV). They have been associated with the vacancy island formation by desorption of a Cd atom from the topmost layer.[7,19] QMS measurements yield an activation energy of (1.98 ± 0.18) eV for congruent sublimation in the higher temperature range between 410 °C and 480 °C,[10] which is also in good agreement with the RHEED results. However, weight loss measurements on a rough CdTe(001) sample show an activation energy of only 1.54 eV in the 300–400 °C temperature range.[11] On the background of the assumption that sublimation occurs in a pure layer-by-layer mode, this difference cannot be explained.

In this paper, we present a combined investigation of the sublimation of CdTe(001) comprising high-resolution low-energy electron diffraction (HRLEED) and quadrupole mass spectrometry (QMS) as well as solid-on-solid (SOS) computer simulations. HRLEED offers the possibility of in-situ spot profile measurement during the sublimation. By evaluating the half widths of the profiles, the step density was determined quantitatively as a function of time.[20,21] Thus, we were able to discriminate the relative contribution of the step flow and the layer-by-layer sublimation process that is equivalent to a determination of the small fraction of desorbing atoms that create new steps. Additionally, the kinetics of sublimation oscillations as well as mass desorption were studied by temperature dependent QMS and HRLEED measurements on *identically prepared* samples.

For a better understanding of the underlying microscopic processes the time evolution of the surface morphology was modeled by kinetic Monte Carlo (KMC) simulations on the basis of the solid-on-solid (SOS) model. For these model surfaces LEED profiles have been calculated in the kinematic approximation, and the desorption flux was monitored. The SOS model is ideally suited to relate the ‘‘macroscopic effects’’ observed in the experiment to the underlying ‘‘microscopic processes’’ on atomic scale. Even though some analytical descriptions for nonequilibrium processes on surfaces exist, they are limited to rather special situations,[22] and therefore computer simulations are an important tool to study nonequilibrium situations.[23] SOS-models have already been successfully applied to diverse surface processes as sputtering,[24,25] layer-by-layer and step-flow growth,[26] or the three-dimensional growth mode in MBE.[27] Recent computer simulations also considered (amongst other effects) the effect of desorption during growth[2,28,29] and sublimation.[8]

II. EXPERIMENT

The samples were undoped CdTe(001) substrates with a miscut of $<0.25°$ (Japan Energy Corporation). The temperatures were measured by a Cromel-Alumel thermocouple attached to the sample holder and controlled within an error of ±0.5 K. Systematic temperature errors are estimated to be $\leqslant 5$ K. The surface preparation was done by sputtering for 10 min with Ar^+ ions at an energy of 600 eV and subsequent annealing at 320 °C for 10 min. This preparation routine removes all surface contamination and yields atomically flat terraces with average widths of several hundreds of Å.[30,31] Sublimation was studied by quickly (<1 min) heating the sample from lower temperatures (at which sublimation is negligible) (250 °C–270 °C) to a temperature in the sublimation regime (300 °C–340 °C). The LEED intensities and spot profiles were recorded at constant temperature, using a HRLEED instrument with a transfer width of 1800 Å.[30]

Cd and Te partial pressures were measured with a quadrupole mass spectrometer (Balzers QMS 421) in line of sight to the sample surface. The desorption flux was measured relative to the background, which was determined while keeping the sample at 250 °C. For the measurements the sample was heated to constant sublimation temperatures (330 °C–360 °C) for 5 min and then cooled down again to 250 °C. In comparison to measurements with linear temperature ramps, this procedure was found to be more accurate because the background pressure due to desorption from the sample holder could be discriminated from the desorption signal from the sample. All experiments were done in UHV conditions at a base pressure below 2×10^{-10} mbar.

III. EXPERIMENTAL RESULTS

A. HRLEED measurements

During the sublimation process a HRLEED pattern with pronounced integral order spots and unchanged symmetry with respect to the structure observed at room temperature was observed, which shows that the surface remains crystalline throughout the sublimation process. The surface was (2×1) reconstructed, the superstructure spots being strongly elongated along the [110] direction, due to the formation of asymmetric domains as described in Ref. 32.

The time evolution of the average step density was measured by successively recording the peak intensity as well as spot profiles of the specular spot ((0,0)) in [110] and $[1\bar{1}0]$ direction during the sublimation process. An electron energy of 45 eV was chosen. This causes destructive interference of electrons scattered from adjacent terraces separated by steps of 3.3 Å height (*antiphase condition*), which is known to be the predominant step height on CdTe(001).[30,31,33] We note that for this electron energy a maximal amplitude of the peak intensity oscillations during sublimation was found.[31]

Figure 1 shows the specular spot profiles recorded in [110] and $[1\bar{1}0]$ direction at the first maximum of the intensity oscillation observed at 310 °C (i.e., after 750 *s* in Fig. 2). The spot profiles exhibit almost identical half widths in the two directions described above. Additional two-dimensional scans (not shown here) show that the specular spot is almost round, revealing a nearly isotropic terrace length distribution. The profiles were fitted by a so-called *modified Lorentzian*

$$L_{3/2}(k_{\parallel})=\frac{I_0}{[1+(k_{\parallel}\Gamma/2)^2]^{3/2}}, \tag{1}$$

and the average terrace width Γ was derived from the fits of Eq. (1) to the experimental profiles. This type of spot profile is expected in two dimension (2D) for a geometrical terrace width distribution, i.e., for a constant step probability.[34] Instrumental broadening was included in the fit by a numerical convolution with a measured instrumental response function. As shown in Fig. 1 the experimental profiles (dots) are very well reproduced by the parameter fits (lines), which shows that the surface morphology can be well described by a geo-

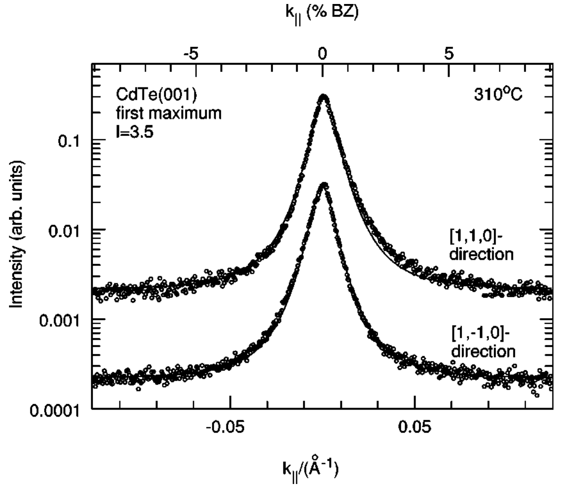

FIG. 1. Specular spot profiles recorded in $[110]$ and in $[1\bar{1}0]$ direction in the first intensity maximum at about 550 s after the onset of the sublimation at 310 °C (see Fig. 2). The electron energy was 45 eV, corresponding to destructive interference from adjacent terraces. Fits to the data according to Eq. (1) plus a linear background are shown as solid lines. (The profiles are vertically shifted for clarity.)

metrical terrace width distribution. The fits yield almost identical average terrace widths in the $[1\bar{1}0]$ and in $[110]$ direction of 287 and 275 Å, respectively.

Since all recorded profiles during the sublimation process could be well fitted by Eq. (1), the step density Γ^{-1} and the peak intensity I_0 could be tracked quantitatively by analyzing all measured spot profiles in an identical manner. Figure 2 shows the fit results of such a profile series. These measurements were carried out at a constant temperature of 310 °C. Upon the onset of sublimation, correlated oscillations of the peak intensity I_0 *and* of Γ are observed. This reveals, that the intensity oscillations are indeed caused by an oscillating step density. However, the amplitude of the oscillations of Γ is very small on a large constant background. This background should be due to permanent steps related to the intrinsic surface morphology. The average terrace width varies from ≈ 250 Å *in the first minimum* to ≈ 290 Å *in the first maximum* of I_0. This relative change of only 15% shows that the intensity oscillations are caused by small changes of an almost constant step density. This can be explained by the nucleation of an only small number of *polyvacancies* (vacancy islands or ‘‘Lochkeime’’)[4,5] in the uppermost layer by the desorption of Cd and Te atoms. Once the polyvacancies have nucleated they grow by step flow sublimation until they coalesce with other vacancy islands or step edges. However, this process causes only a small minority of additional steps on the sublimating surface.

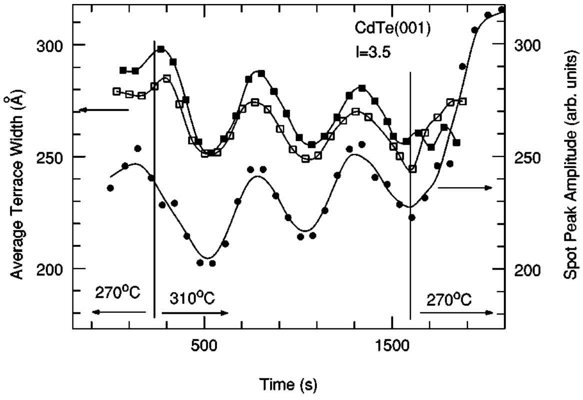

FIG. 2. Time evolution of the specular spot intensity I_0 (right scale) and the average terrace width Γ (left scale), as determined by the parameter fits described in the text (see also Fig. 1). Empty squares: $[1\bar{1}0]$ direction, full squares: $[110]$ direction. The solid lines are guides to the eye.

The fact that all recorded profiles are of identical form shows that the polyvacancy formation does only cause minor deviations from the geometrical terrace width distribution. Based on this finding a rough estimate of the increase in the density of steps caused by vacancy island nucleation can be given by simply subtracting the minimal from the maximal observed step density.[31] For the data presented here, this calculation yields an average distance of ≈ 2000 Å between the additional steps related to the polyvacancies.

The common picture of layer–by–layer sublimation implies the growth and coalescence of polyvacancies. However, all steps on the surface, whether permanent or caused by the polyvacancies, should contribute equally to the desorption flux.[35] Therefore, a dominant contribution from the step flow to the total sublimation rate can be derived from the non-oscillating part (background) of the step density.

B. Comparison with QMS measurements

As a consequence the desorption flux is dominantly related to the speed of the step flow and not by the rate of polyvacancy nucleation. The two processes are governed by different microscopical mechanisms and therefore should exhibit different kinetics.[8] In order to determine the mass desorption flux separately, additional QMS measurements were performed.

Figure 3 shows an Arrhenius plot of the Cd and Te partial pressures as well as of the intensity oscillation frequency monitoring the polyvacancy formation rate. The data were obtained from identically prepared samples. All three data sets are well described by Arrhenius laws of the form: exp $(-E_A/k_B\,T)$ (solid lines). Hereby, we do not find a difference in the activation energies E_A for the mass desorption flux of Cd and Te, indicating that no preferential desorption of Cd from the bulk occurs as has been observed in Ref. 10. This could be related to slightly modified bulk stoichiometry in Ref. 10, due to a different sample treatment such as additional annealing procedures.

C. Experimental conclusions

Two significantly different activation energies are found for the mass desorption flux $(1.55 \pm 0.10$ eV) and for the HRLEED oscillation frequency $(1.94 \pm 0.10$ eV) in Fig. 3. It reveals that the processes responsible for the mass desorption and for the intensity oscillation frequencies indeed exhibit different kinetics and are thus to some degree independent.

This observation can be explained by the dominant step flow contribution to the total mass desorption, whereas the electron diffraction oscillations are selectively determined by the formation and coalescence of polyvacancies. This is in accordance with the observation of only small oscillations of

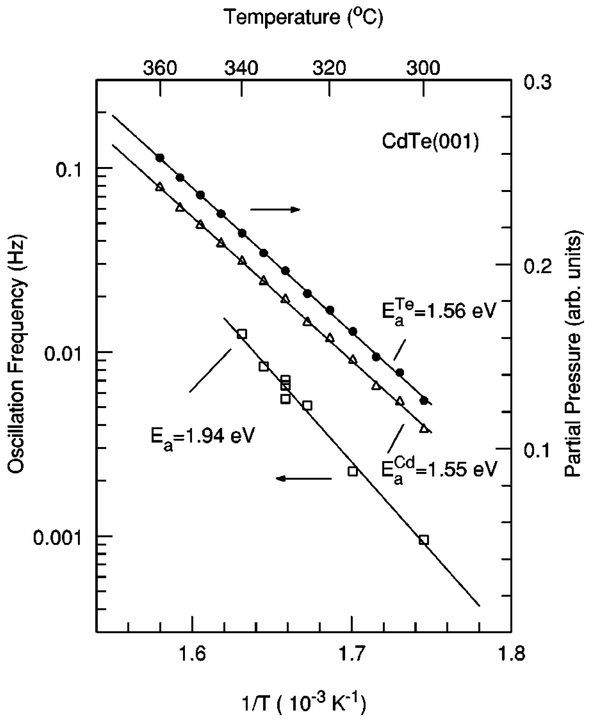

FIG. 3. Arrhenius-plot of the specular spot oscillation frequency (squares) as well as the Cd (triangles) and Te (circles) desorption rates measured by QMS. The solid lines are best fits to an Arrhenius law.

the intensity as well as the step density Γ^{-1}. It also explains that *two different* activation energies have been obtained in previous investigations for the desorption flux[11] and the RHEED intensity oscillation frequencies[1,7,9] in the same range of temperatures.

IV. SOLID-ON-SOLID SIMULATIONS

The above presented experimental investigation seems to indicate the presence of a rather special situation for the sublimation of CdTe(001). In order to test and visualize the scenario developed in the preceding section we used computer simulations in the framework of the SOS model, the basic approach that was described in Refs. 26 and 36. The simulations will show however that the observed behavior is not a specific property of CdTe(001) alone but constitutes a very general behavior that is already observed in the simplest model of surface kinetics.

A. Computational model

The model possesses two basic restrictions: (a) the lattice structure is fixed and (b) no overhangs are allowed. In the model used in this paper, only one species of atoms is simulated on a simple cubic lattice. This can be interpreted as the simulation of the Cd atoms with slower dynamics (responsible for the Cd-terminated surface[32]). The Te-atoms can be assumed to be in thermal equilibrium, thus affecting the Cd dynamics in a mean-field manner. Therefore, a qualitative understanding of the kinetics is well within the scope of this model.[24,25,27] For well-chosen experimental conditions and carefully adjusted energy parameters in the simulations, even a quantitative agreement between experiments of compound semiconductors and simulations can be achieved.[26]

The particles are allowed to diffuse with a rate $\gamma = \nu_0 \exp(-E/k_B T)$ for a jump in each direction. The vibration frequency is chosen to be of the order of typical Debye frequencies $\nu_0 = 10^{12} s^{-1}$. The activation energy is parameterized as $E = E_B + n \cdot E_N$ where E_B stands for the diffusion barrier of an atom on a flat surface. Each next in-plane neighbor of the considered atom contributes E_N to the activation energy. Hereby, n denotes the number of next in-plane neighbors. The term $n \cdot E_N$ thus describes the energy required to break the bonds to n neighboring atoms. Furthermore, an Ehrlich-Schwoebel barrier at step edges E_S is considered.[37,38] This parameterization of the activation energy is commonly used in KMC simulations.[24,26] A second process is the desorption of particles. A particle with n next in-plane neighbors possesses a desorption rate $\nu_0 \exp[-(E_D + n \cdot E_N)/k_B T]$.

The simulations were carried out on a 512×512 lattice with helicyclic boundary conditions. We will measure all length scales on the substrate in units of the lattice constant (a). The height will be expressed in monolayers (ML). All results were obtained from averaging 6 independent simulation runs. The model parameters were chosen as follows: $E_B = 0.9$ eV, $E_D = 1.1$ eV, $E_N = 0.25$ eV, and $E_S = 0.1$ eV. This particular choice of parameters leads to length and time scales that are of the same order as the experimental findings presented in this paper. However, we would like to stress that the findings of our present paper are of more general relevance, independent of the specific choice of the energetic parameters.

An earlier investigation[8] of stepped surfaces with parallel terraces of equal width L (vicinal surfaces) performed with this model showed a strong influence of the morphology on the sublimation process. Desorption from surfaces with terraces larger than a critical terrace width $L_\times$ gave layer-by-layer oscillations whereas on small terraces $(L < L_\times)$ no formation of polyvacancies was found. For the above set of parameters we found $L_\times \approx 93\,a$ at 327 °C (600 K), which increases with decreasing temperature. A significant step flow in combination with intensity oscillations, however, was *not* observed. This appeared to be a general property of regularly stepped vicinal surface.

Here, we went one step further and instead of one unique terrace width we used a vicinal surface with an approximately[39] geometric distribution of terrace widths with parallel step edges (in correspondence to the Lorentzian shape of the LEED profiles). The average terrace width was set to $34a$. We note that on real surfaces rather an assembly of extended mounds and dislocation-induced spirals is often observed.[40] Since the LEED-instrument exhibits a transfer width much smaller than the typical size of such mounds,[30] the modeled vicinal surface should thus be sufficient to represent the real surface.

B. Computational results

Figure 4 shows a sequence of snapshots of the simulated surfaces at 327 °C. Hereby Fig. 4(a) corresponds to the first minimum and 4(c) to the maximum of the LEED intensity in Figs. 5 and 6. Clearly, both processes are present: step flow

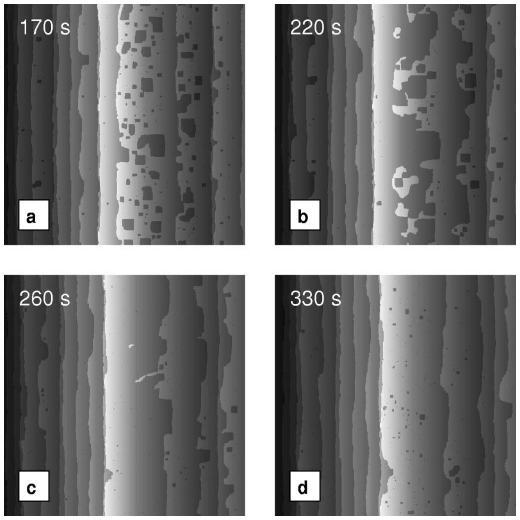

FIG. 4. Snapshots of simulated surfaces on a 512×512 lattice at 327 °C. We show a complete sequence starting from the first minimum in the LEED intensity (a) where on the large terraces a large number of vacancy islands exists. In (b) the coalescence of polyvacancies is shown which evolves to a smooth surface with maximal LEED intensity (c). In (d) the creation of new polyvacancies can be identified. (For the visualization the grey scale on the terraces is tilted). Note the movement of the steps with respect to the lettering, which marks a constant position.

as well as creation [Fig. 4(d)] and coalescence [Fig. 4(b)] of polyvacancies. We note that such a polyvacancy formation was recently also observed by scanning tunneling microscopy (STM) on a CdTe(001) sample heated shortly to 320 °C.[41] Note that the two processes occur in different local areas on the surface: creation and coalescence of polyvacancies occurs on large terraces only, whereas step flow is the only process on small terraces. The influence of the adatom gas can be easily recognized. On the large terraces one can see that near the step edges no polyvacancies are formed. The high concentration of the adatom gas near step edges leads quasi to a ‘‘passivation’’ of the terraces and suppresses the vacancy nucleation. This is the reason, why only step flow occurs on the small terraces. One could speculate that another reason also leads to the suppression of polyvacancy formation on small terraces: if the step velocity were high enough there would be not enough time for the formation of polyvacancies. In the simulations, however, the step velocity is rather small and thus only the passivation by the adatom gas plays a role.

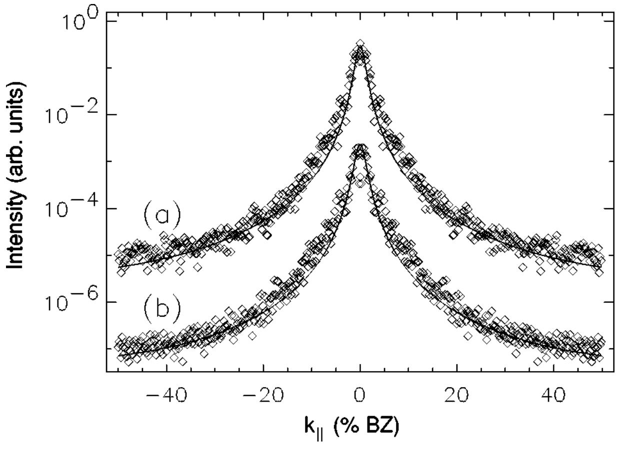

FIG. 5. Spot profiles of simulated surfaces. The lower curve (b) corresponds to the first minimum and the upper one (a) to the first maximum of I_0. For clarity the two curves are shifted against each other. The lines are nonlinear least-square fits according to Eq. (1) plus a linear background, excluding the central point at $k_{\|}=0\%$ BZ, which is not shown here.

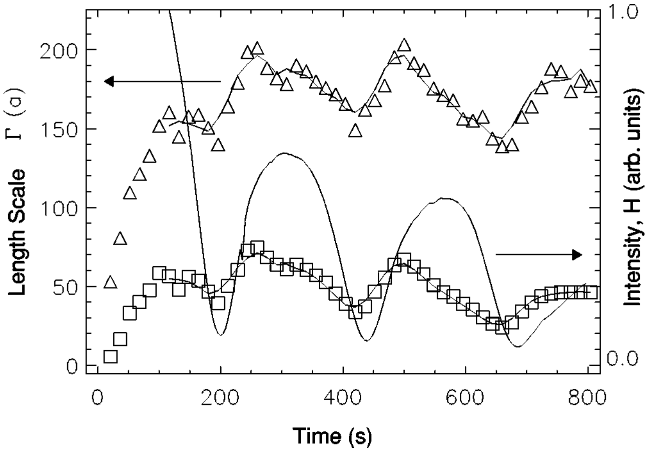

FIG. 6. Intensity $I_0(\square)$ and typical length scale $\Gamma(\triangle)$ as derived from fits of Eq. (1) to the simulated profiles. The solid lines are guides to the eye. Note that at $t=0\ s$, both I_0 and Γ are not at maximal values as expected for the smooth starting surface with perfectly aligned step edges. This is due to the fact that the fit to the modified Lorentzian breaks down at $t=0\ s$, because the profile is composed of a δ-function and a *nonmodified* Lorentzian profile. In addition the spot intensity at $k_{\|}=0$ (the mean reduced height H, full line) is shown. (For further details see text.)

For these surfaces we calculated LEED profiles within the kinematic approximation. Under antiphase condition this is equivalent to taking the Fourier transform of a surface where all heights are reduced to 1 for even, and −1 for odd heights. The squared absolute value of the Fourier transform at wavevector $k_{\|}$ is then proportional to the intensity of a LEED measurement $I(k_{\|})$. From the definition of the Fourier transformation it follows that the intensity at $k_{\|}=0$ describes the mean height H of the reduced surface. A step train moving at a constant velocity does not change this quantity (except for possible boundary effects[42]) whereas the creation of polyvacancies does. Hence, oscillations of H directly monitor the creation and coalescence of vacancy islands. On the other hand, all wavelength dependent information is contained in $I(k_{\|}\neq 0)$, which is comparable to the information obtained from the HRLEED spot profiles. Thus, only the points for $k_{\|}\neq 0$ were used in the analysis of the simulated data by the profile [Eq. (1)]. The noise (which is solely due to the randomness of the Monte Carlo algorithm—and not due to ‘‘conventional’’ background noise as in the experiment) leads to an offset of the whole profile,[43] which we considered in the fits by an additional constant.

Clearly, the simulated diffraction profiles are strongly anisotropic due to the enforced step direction. Therefore, we calculated the average of the k_x and k_y scans $\{I(k_{\|})=1/2\cdot[I(k_x)+I(k_y)]\}$ in order to obtain results comparable to the experiment, in which both step edge orientations appear with approximately equal probability. The resulting profiles for the first minimum and maximum of the intensity are shown in Fig. 5. These simulated profiles are also well described by the modified Lorentzian [Eq. (1)] as the experimental data. We are aware that the underlying assumption of an isotropic terrace width distribution, which leads to Eq. (1) (Ref. 34) is not strictly fulfilled here. However, we observed that after an initial step roughening the *modified* Lorentzian constitutes a considerable better fit to the data than the *non-modified* Lorentzian

$$L(k_\parallel)=\frac{I_0}{1+(k_\parallel\Gamma/2)^2}. \tag{2}$$

We also note that the starting surfaces with perfectly straight step edges are not described by Eq. (1) because the k_y scans yield a δ function and the k_x scans a *non modified* Lorentz profile.

We now turn to the dynamics of the sublimating surfaces simulated at $T=327$ °C. As in the HRLEED experiments, we observe oscillations in the intensity and in the width of the simulated profiles (see Fig. 6). After an initial step roughening the mean reduced height H, the intensity I_0, and the length Γ from the fit of the profiles to Eq. (1) oscillate in phase. [Hereby, the singular point $H=I(k_\parallel=0)$ was excluded from the fit.] The oscillations of I_0 and Γ are slightly asymmetric (as trendwise also seen in the experimental data in Fig. 2), which indicates that the polyvacancy decay (by coalescence) is faster than their nucleation. Note, that $\Gamma\sim 180\,a$ is rather large compared to the preset average terrace width of $34\,a$ of the vicinal surface. This is due to the fact that the profiles were averaged in the directions parallel and perpendicular to the step direction (see above). The same considerations should apply to the experimental observation of $\Gamma\sim 270$ Å, which corresponds to ~60 lattice constants of CdTe(001) ($a_{\mathrm{CdTe}}=4.58$ Å). In the following, we have used the mean reduced height H in order to extract oscillation periods, since it is the statistically most robust quantity (compared with the fit parameters I_0 and Γ).

As in the experiments we compare the oscillation frequency with the mass desorption flux as a function of temperature. Figure 7 shows that the two quantities exhibit a different temperature dependence. The overall mass desorption flux (dm/dt) is described by a lower activation energy compared to the intensity oscillations. A fit of dm/dt to an Arrhenius behavior yields the relation

$$\frac{dm}{dt}=2.94\cdot 10^{11}\exp(-1.63\,\mathrm{eV}\mathrm{k_B}T)\ \mathrm{ML\,s^{-1}}, \tag{3}$$

which agrees within the error limit with the previously obtained results for vicinal surfaces in the free step-flow regime[8]

$$\frac{dm}{dt}=\frac{v_{\mathrm{step}}}{L}=1.26\cdot 10^{11}\exp(-1.60\,\mathrm{eV}/\mathrm{k_B}T)\ \mathrm{ML\,s^{-1}}. \tag{4}$$

Here, the step velocity v_{step}, as derived in Ref. 8, with $L=34$ was used. Similarly, the temperature dependence of the oscillation rate

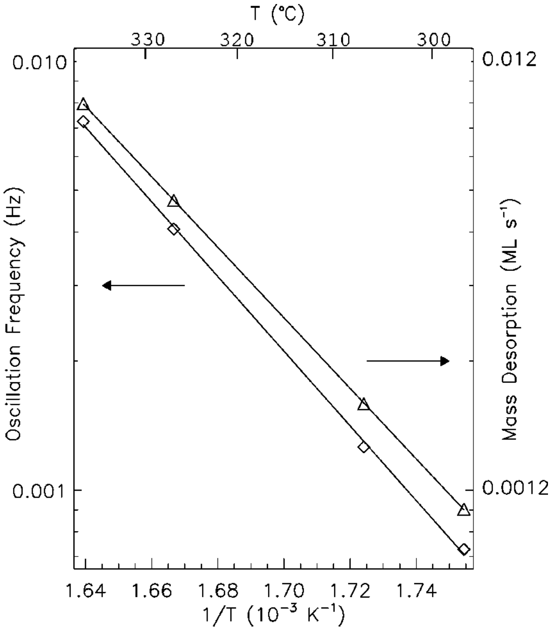

FIG. 7. Arrhenius plot of the mass desorption (△) and the oscillation frequency (◇). The solid lines are fits which yield activation energies of 1.63±0.02 eV (mass desorption) and 1.73 ±0.02 eV (oscillations). Statistical errors are less or equal to the sizes of the symbols.

$$\frac{1}{\tau}=1.35\cdot 10^{12}\cdot\exp(-1.73\,\mathrm{eV}/\mathrm{k_B}T)\ \mathrm{s^{-1}} \tag{5}$$

agrees very well with that expected on the basis of earlier simulations of nonstepped (singular) surfaces.[8]

The difference in the here obtained activation energies for mass desorption ($E=1.63\pm 0.02$ eV) and oscillation frequency ($E=1.73\pm 0.02$ eV) of about 0.1 eV in Eqs. (3) and (5) can be understood by the ''expensive'' creation of vacancies, for which a surface atom has to break four bonds to the next in-plane neighbors.[8] In addition, the Ehrlich-Schwoebel barrier also dominantly influences the creation of the polyvacancies. Even though it is evident that the used parameterization cannot describe all details of vacancy formation on the CdTe(001) surface (e.g., the correct details related to the surface reconstruction[32]), the qualitative explanation correctly reproduces the trend of the experimental results. In order to adapt the computational model better to the difference of the measured experimental activation energies one should thus increase the binding energy and/or the Ehrlich–Schwoebel barrier.

Our simulations were however confined to the here investigated temperature range of $T=295$ °C–340 °C. At lower temperatures, the minimal terrace width necessary for vacancy formation $L_\times$ becomes too large and the intensity oscillations are thus too weak to be detected. At higher temperatures the mass desorption flux dm/dt becomes comparable to *one* monolayer/τ, indicating that mass desorption is solely due to creation and coalescence of polyvacancies. In this case, the mass desorption rate should coincide with the rate calculated from intensity oscillations. This is in agreement with the experimental finding that mass desorption at very high temperatures (410 °C–480 °C) is characterized by the same activation energy[10] as that observed in diffraction experiments at lower temperatures (300 °C–400 °C).[1,7,9]

V. CONCLUDING DISCUSSION

We have experimentally determined activation energies for the desorption flux (1.55 ± 0.1 eV) and for the HRLEED oscillation frequency (1.94 ± 0.1 eV) on CdTe(001). This significant difference is consistently explained with the above presented model of a step-flow-dominated mass desorption and polyvacancy nucleation dominated sublimation oscillations. Additional LEED measurements during sublimation at 330 °C (not shown here)[44] have yielded a considerably reduced average distance (about 800 Å) between steps caused by vacancy islands compared to 2000 Å at 310 °C. Therefore, at higher temperatures, the oscillating contribution of step density is expected to exceed the constant contribution, thus causing a transition to a layer-by-layer sublimation dominated desorption flux.[4,5] The Arrhenius law is no longer expected to be valid in this transition regime.

The SOS model simulations illustrate that the two desorption mechanisms do indeed compete simultaneously but in regions with locally different terrace sizes. For most terraces step flow is observed, but in addition, on very large terraces ($L>L_\times$), the creation of vacancy islands occurs, too. On smaller terraces this process is suppressed by the higher density of the adatom gas. As a consequence the *simultaneous* occurrence of step flow and vacancy island creation/coalescence is related to the wide distribution of terrace widths, and such a behavior can be also expected for other surfaces of other materials with comparable terrace width distributions, too.

It is of course an interesting question which microscopic process is the most responsible one (rate limiting) for the observed difference of the activation energies between step-flow sublimation and polyvacancy nucleation. At this point, we recall a microscopical analysis of the effective sublimation energies which we derived earlier from our KMC simulations.[8] This analysis revealed that the effective energy for sublimation is related linearly to *all* (quasi-)microscopic energies ($E\mathrm{sub}=\alpha_B E_B+\alpha_D E_D+\alpha_N E_N+\alpha_S E_S$). The KMC simulations on vicinal surfaces showed that free step flow is characterized by $\alpha_B\approx0.70$, $\alpha_D\approx0.32$, $\alpha_N\approx2.4$, and $\alpha_S\approx0.21$. We found that the change from the step-flow sublimation to the layer-by-layer sublimation mode causes a distinct change of the coefficients α_N and α_S and only a slight change of α_B and α_D ($\alpha_B\approx0.61$, $\alpha_D\approx0.35$, $\alpha_N\approx2.85$, and $\alpha_S\approx0.44$). The change in α_N is plausible because the creation of vacancies requires to break a higher number of bonds with respect to creation of free adatoms at step sites. The increased influence of the Ehrlich-Schwoebel barrier can be also related to its importance for vacancy creation: In order to leave a vacancy island an adatom first has to overcome the Ehrlich-Schwoebel barrier whereas for the step flow E_S only induces an asymmetric detachment from steps.

This above mentioned analysis demonstrates also, that the different sublimation energies *cannot* be interpreted as a difference of two single microscopic energies that are rate limiting energies in the two different sublimation regimes. This can be understood from the fact that the adatom gas plays an important role for the sublimation. It does for example (see above) suppress the nucleation of vacancies near steps. Through this mechanism the desorption energy into the vacuum and the one from steps (which controls the the density of the adatom gas on terraces) indirectly determine the probability of vacancy nucleation. However, when large island vacancies are created, these islands evolve essentially via-step flow sublimation, i.e., detachment from steps and subsequent desorption, too, until coalescence occurs. As a consequence the processes leading to step flow and layer-by-layer sublimation are intimately coupled to each other and cannot be understood from single-rate limiting processes.

VI. SUMMARY

To summarize, we have shown that the sublimation rate of CdTe(001) depends on sample morphology, i.e., step density, as well as temperature in a complicated manner and cannot be described by one single activation energy. Using HRLEED and QMS we were able to distinguish two different modes of sublimation, which are simultaneously present: (a) the nucleation and coalescence of polyvacancies and (b) step-flow sublimation. The computer simulations of the SOS model showed that the presence of a geometric terrace width distribution is already sufficient to allow both, formation of polyvacancies and step flow in regions with low and high step densities, respectively. The relevant length scales for the two modes, i.e., the vacancy distance compared to the terrace width distribution are comparable in a limited temperature range, which is essential for the observation of both sublimation modes.

Our results explain the striking difference of activation energies for the desorption flux and for the oscillation frequencies in diffraction measurements reported for CdTe(001). The sublimation is found to be step flow dominated in the temperature range from 300 °C to 360 °C and average step distances are of some 100 Å with an activation energy of ≈1.55 eV. For higher temperatures as well as for much larger average terrace widths, the importance of polyvacancy formation is expected to increase and should become the dominating process, yielding activation energies of ≈1.9 eV, in agreement with Ref. 10.

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