Comment on "Determination of Interlayer Diffusion Parameters for Ag/Ag(111)"

In a recent paper Roos and Tringides argue [1] that the ratio of the prefactors ("attempt frequencies") ν_s and ν_t for hopping over a step edge and hopping on a terrace, respectively, can be accurately determined for Ag/Ag(111). They report the value $\nu_s/\nu_t = 10^{2.0\pm0.3}$ based on three different ways of analysis. However, all three distinct methods assume a definite value $\Delta E_S = 130$ meV for the additional step edge barrier that according to recent theoretical developments [2–4] cannot be trusted with confidence. Based on the available low temperature data (100–200 K), one can deduce $\nu_s/\nu_t \gg 1$ (when presuming a commonly accepted value $\Delta E_S \geq 120$ meV), but the specific value for ν_s/ν_t depends on the way of data analysis.

The determination of ΔE_S is a long-standing challenge, in particular for elements not accessible by field ion microscopy. To solve the problem, various methods have been developed by applying different experimental techniques [e.g., scanning tunneling microscopy, low energy electron microscopy, reflection high-energy electron diffraction (RHEED)]: (i) Monitoring the decay of multilayer islands at high temperatures T [5], (ii) investigating the occurrence of second layer nucleation in dependence of the island size [6], (iii) studying the completion of successive layers building a type of "wedding cake" [7], (iv) fitting the activation energy for the initial RHEED peak intensity decay rate to the result of kinetic Monte Carlo simulations [8], and (v) applying the concept of a critical nucleation density [7,9] (for a criticism of this concept see, however, [3]). All these methods determine essentially the quantity $(\nu_s/\nu_t)\exp(-\Delta E_S/k_B T)$, so that separating ν_s/ν_t from the Boltzmann factor requires analyzing data for different T.

Data for Ag/Ag(111) allowing this kind of analysis were published by Bromann *et al.* [6]. These authors determined, for different temperatures T, the fraction $f(t)$ of islands on top of which a stable cluster has nucleated after time t of evaporation. The fraction $f(t)$ depends on the rate $\Omega(t)$ for second layer nucleation, which in turn is strongly affected by $\Delta E_S/k_B T$. By employing theoretical results for $\Omega(t)$, the measured $f(t)$ have been fitted for two different T, and thereby $\Delta E_S \cong 120$ meV and $\nu_s/\nu_t \cong 50$ were extracted (the 120 meV were later changed to 130 meV by a refined analysis of the same data [10]).

The analysis of Bromann *et al.* (as well as that in [10]) was based on $\Omega(t)$ derived from a theory by Tersoff *et al.* [11]. However, it was shown recently that the validity of this theory is limited to critical nuclei of size $i > 2$, or to small step edge barriers for $i = 2$ [4]. For $i = 1$, as it is the case in the Ag/Ag(111) system, the second layer nucleation is governed by fluctuations, which yield a modified $\Omega(t)$ [2–4]. Therefore, it was suggested [2] to reexamine the experiment by Bromann *et al.*

This reexamination has been carried out recently as part of the work by Krug *et al.* [3]. By using both ν_s/ν_t and ΔE_S as free fitting parameters, one obtains $\Delta E_S \cong 320$ meV and $\nu_s/\nu_t \cong 4 \times 10^8$, i.e., much larger values than the previous ones. One might object that these results are in disagreement with effective medium calculations [12], as well as with results from evaluating other experimental data [7–9]. However, in all these evaluations a particular fixed value for ν_s/ν_t is *assumed.*

When assuming some fixed value for ν_s/ν_t in the analysis of the data of Bromann *et al.,* one has to allow for a temperature dependence of ΔE_S. Such a dependence is conceivable when remembering that ΔE_S is an effective barrier, which results from an averaging over microscopic rates. Setting $\nu_s/\nu_t = 1$, Krug *et al.* obtained $\Delta E_S(T = 120\text{ K}) \cong 110$ meV and $\Delta E_S(T = 130\text{ K}) \cong 100$ meV [3] that are values comparing more favorably with the alternative ways of determination referred to above.

In summary, based on the existing data for Ag/Ag(111) a definite value for ΔE_S (and thus ν_s/ν_t) cannot be given, but the low temperature data yield $\nu_s/\nu_t \gg 1$ for $\Delta E_S \geq 120$ meV. In order to obtain better results for ΔE_S and ν_s/ν_t, one could perform RHEED measurements at different temperatures and thereby extend the detailed analysis by Roos and Tringides [1].

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[1] K. R. Roos and M. C. Tringides, Phys. Rev. Lett. **85**, 1480 (2000).
[2] J. Rottler and P. Maass, Phys. Rev. Lett. **83**, 3490 (1999).
[3] J. Krug, P. Politi, and T. Michely, Phys. Rev. B **61**, 14 037 (2000).
[4] S. Heinrichs, J. Rottler, and Ph. Maass, Phys. Rev. B **62**, 8338 (2000).
[5] M. Giesen and H. Ibach, Surf. Sci. **431**, 109 (1999).
[6] K. Bromann, H. Brune, H. Röder, and K. Kern, Phys. Rev. Lett. **75**, 677 (1995).
[7] J. A. Meyer, J. Vrijmoeth, H. A. van der Vegt, E. Vlieg, and R. J. Behm, Phys. Rev. B **51**, 14 790 (1995).
[8] K. R. Roos, R. Bhutani, and M. C. Tringides, Surf. Sci. **384**, 62 (1997).
[9] P. Šmilauer and S. Harris, Phys. Rev. B **51**, 14 798 (1995).
[10] K. R. Roos and M. C. Tringides, Surf. Rev. Lett. **5**, 833 (1998).
[11] J. Tersoff, A. W. Denier van der Gon, and R. M. Tromp, Phys. Rev. Lett. **72**, 266 (1994).
[12] Y. Li and A. E. DePristo, Surf. Sci. **319**, 141 (1994).

