Nonclassical "Explosive" Nucleation in Pb/Si(111) at Low Temperatures

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Classically, the onset of nucleation is defined in terms of a critical cluster of the condensed phase, which forms from the gradual aggregation of randomly diffusing adatoms. Experiments in Pb/Si(111) at low temperature have discovered a dramatically different type of nucleation, with perfect crystalline islands emerging "explosively" out of the compressed wetting layer after a critical coverage $\Theta_c = 1.22$ ML is reached. The unexpectedly high island growth rates, the directional correlations in the growth of neighboring islands and the persistence in time of where mass is added in individual islands, suggest that nucleation is a result of the highly coherent motion of the wetting layer, over mesoscopic distances.

Nucleation is a fundamental process in nature that relates to a wide range of physical phenomena of both basic and technological importance in physical and biological sciences and engineering [1–6]. Many practical applications depend on the nucleation and growth of novel phases with unusual structural and electronic properties, relevant for catalysis and energy conversion. Nucleation involves the fine interplay between equilibrium and nonequilibrium physics, so it also relates to fundamental questions in statistical mechanics [7–12]. Although a complete understanding of nucleation has not yet been attained, the widely used paradigm is based on the model of classical nucleation. The main concept of the model is the existence of a critical size cluster r_c, which defines the minimum cluster size, such that clusters larger than r_c are stable and do not dissociate. The mass needed for the clusters of the condensed phase to grow is provided by diffusing adatoms within the initial homogeneous dilute phase. This analysis has been applied universally for a wide range of physical systems and especially to the epitaxial growth of ultrathin films [13–15].

In particular, island nucleation is observed in strained systems, a result of a morphological 2D-to-3D transition commonly referred to as the Stranski-Krastanov (SK) growth mode. The competition between strain energy (due to the lattice mismatch between overlayer and substrate) vs the surface energy drives the transition. Depending on the lattice mismatch ε between the substrate and the film different pathways are possible for the 3D transition. For small ε, 3D islands nucleate above a critical thickness h_c with misfit dislocations decorating the interface, but for larger ε, roughening of the film is possible at much lower film thickness than h_c [16]. For Pb/Si(111) no roughening is observed. These predictions have been fully confirmed in the prototype system $Si_{1-x}Ge_x$ since ε can be varied extensively as a function of stoichiometry [16].

In all SK systems mass transport is through normal random walk diffusion. The detailed study of SK growth at lower temperatures and the role different nonthermodynamic factors can play are not fully explored. Pb/Si(111) follows a similar 2D-to-3D transition and strain is also a key factor (because of the 11% lattice mismatch between Si(111) and Pb(111) as in typical SK systems), but the transition occurs at ~150–250 K. In this work we show that a novel and faster type of nucleation dramatically different from classical nucleation is present. The novel nucleation is not driven by thermodynamic factors but by a very unusual type of mass transport. Pb(111) islands are not built gradually from the sequential aggregation of Pb adatoms; on the contrary, the deposited Pb adatoms are continually consumed by the wetting layer, which fully covers the substrate. After the wetting layer reaches a critical value $\Theta_c \approx 1.22$ ML [22% larger than the metallic Pb(111) density] nucleation is very abrupt, with multiheight, crystalline, fully completed islands, with at least ~10^5 atoms each, emerging from the compressed wetting layer. More importantly, mass transport is not the result of classical random-walk diffusion, but involves the collective motion of millions of atoms over mesoscopic scales. This striking result is deduced from the exceedingly high island growth rate when compared to the classical rate, from directional correlations in the growth of neighboring islands and from temporal correlations in the growth direction of individual islands. For Pb/Si(111) the temperature range these unusual phenomena are observed is centered at ~$0.3T_m$, with T_m the Pb melting temperature. Potentially such nucleation phenomena are more universal and not exclusive to Pb/Si(111) if the corresponding temperature "window" is scaled with T_m.
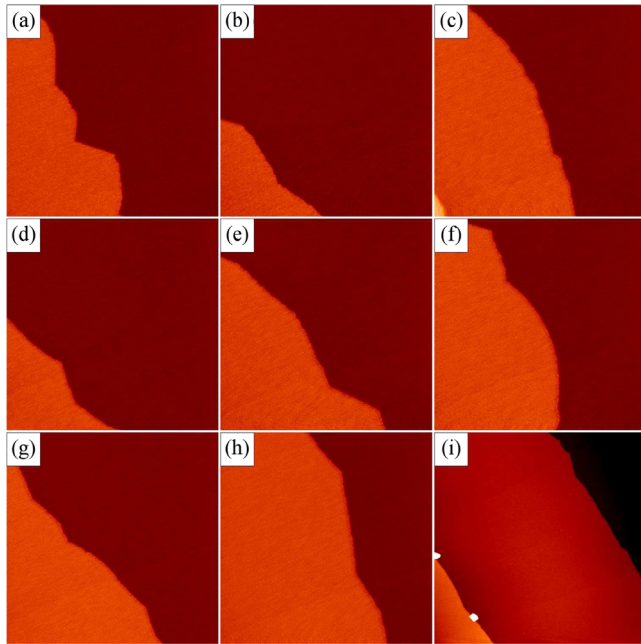
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FIG. 1 (color online). Pb wetting layer evolution on Si(111) − 7 × 7 with Pb deposition at T = 200 K (a) 500 × 500 nm² Θ = 0.82 ML. (b)–(h) 500 × 500 nm² areas after stepwise depositions of ΔΘ ∼ 0.045 ML. (i) Θ = 1.17 ML but the image area is larger, 1500 × 1500 nm².

Experiments are presented here for Pb growth on the Si(111) − 7 × 7 substrate, and similar data have been obtained for growth on the Si(111) − Pb − $\alpha\sqrt{3} \times \sqrt{3}$. Typical results are shown in Figs. 1 and 2. After an initial deposition of 0.82 ML at 200 K, Pb is deposited in smaller stepwise increments of ΔΘ ∼ 0.045 ML (to approach Θ_c with a finer coverage control) and after each deposition, scans of large overlapping areas (their overlap identified by
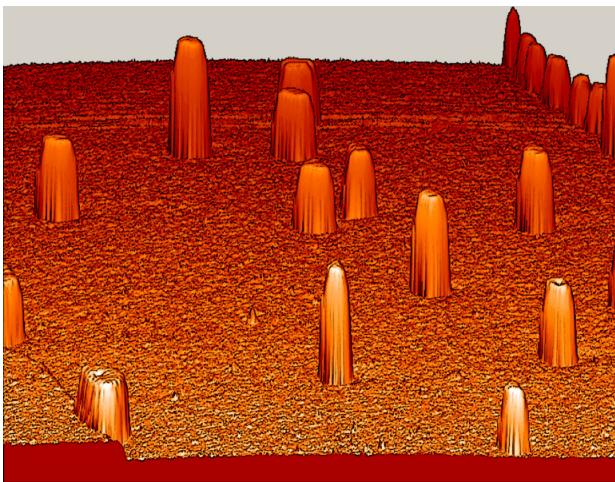

FIG. 2 (color online). 1000 × 1000 nm² Pb on Si(111) − 7 × 7 with several multiheight islands forming at Θ = 1.22 ML by adding ΔΘ ∼ 0.045 ML on the surface of Fig. 1(i). The islands form explosively.

features on the steps) are taken to monitor nucleation changes. Nine images (the first eight are 500 × 500 nm² and the ninth 1500 × 1500 nm²) acquired consecutively are shown in Figs. 1(a)–(i) and no islands are seen [except two small islands nucleated at the step in Fig. 1(i)].

Figure 2 shows the result of one more 0.045 ML deposition in the area of Fig. 1(i). One normally expects to observe the nucleation of small one-layer islands which subsequently grow both in size and height. Because the nucleation and the growth are stochastic processes, the islands are expected to exhibit a wide size distribution that includes a large fraction of small islands. This is not what is observed. Large multiheight (of 4 to 7 layers instead of 1 layer islands) perfect crystalline Pb islands, all above a minimum radius of ∼15 nm, emerge. The island density is very low at 1.65×10^{-5} islands/nm². The ratio $k = (\Delta\Theta_{island})/\Delta\Theta$ of the Pb amount in the islands over the last amount deposited is 2.2, but in other experiments depending on the temperature T, or flux, or how close ΔΘ approaches Θ_c, k can be much higher. This indicates that the nucleation of the Pb islands is completed within the last short deposition in a very "explosive" way.

Although the STM is not the ideal instrument to study kinetics because of the finite acquisition time, which is typically ∼tens of seconds depending on the scan size, one can safely conclude that the nucleation time is less than the STM acquisition time. This is seen from islands encountered earlier in the scan of any size having the same dimensions as islands encountered later in the scan; for fixed temperature the average island size is independent of scan size; under all scanning conditions only completed islands are observed both in the current experiments and in numerous previous experiments carried out by us using both STM and SPA-LEED to study quantum size effects [17]. This conclusion is also very consistent with earlier diffraction experiments with RHEED [18], x-ray [19] and with all three techniques RHEED, x-ray, and He scattering [20] that have shown a steplike intensity increase of the Pb(10) spot, during deposition, after the completion of the wetting layer. From the known flux rates in these diffraction experiments $F \sim 0.9$ ML/min the island nucleation times are extracted to be a few seconds.

In Refs. [18–20] the authors have speculated that high diffusion must be present despite the low temperatures, but its puzzling character was assumed to be still classical. The character of the required mass transport responsible for the explosive nucleation has been identified with further STM experiments shown in Figs. 3(a) and 3(b). The temperature is 200 K and in Fig. 3(a) the coverage is Θ = 1.22 ML; the surface after 3 smaller depositions totaling 0.09 ML is shown in Fig. 3(b). Both imaged areas of Fig. 3 are very large, 1500 × 1500 μm², so mass transport can be checked over mesoscopic distances. Features along the step (i.e., inward kink bottom left) are used to match the y scales in the two images and
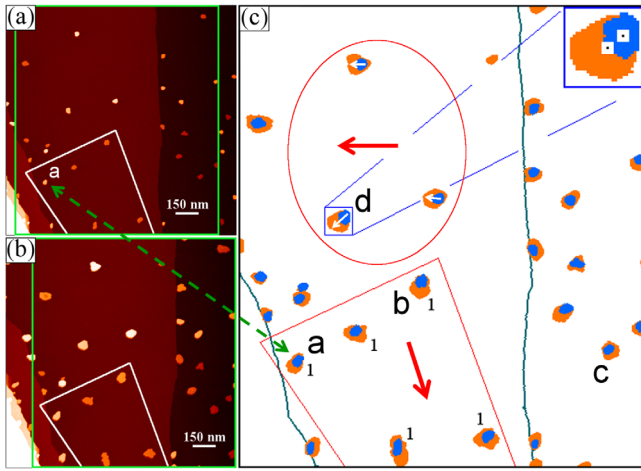
FIG. 3 (color online). Different deposition experiment on Pb/Si(111) − 7 × 7 at 200 K with 1500 × 1500 nm^2 areas imaged sequentially (a) $\Theta = 1.22$ ML. (b) After $\Delta\Theta = 0.09$ ML is added on (a). (c) Overlapping 1320 × 1500 nm^2 sections of (a) and (b) shown in green. In (c) blue shows the areas of the islands in (a) and orange the islands in (b). Inset shows typical large c.m. shift. White arrows indicate islands that paradoxically are growing in the direction of lower adatom influx (if diffusion was classical). The black 1's identify five islands within area A outlined in red in (c) growing in a similar direction indicating correlated transfer of material from the wetting layer to the islands. The same area is shown in white in (a) and (b).

correct for minor nonlinearities of the piezo gain. Figure 3(c) shows the difference between the overlapping areas of Figs. 3(a) and 3(b) so the growth direction for each island can be determined [blue marks the islands in Fig. 3(a) and orange the ones in Fig. 3(b)].

In classical nucleation, islands are expected to grow isotropically since the randomly diffusing adatoms on average arrive with equal probability from all directions [13–15]. The center of mass (c.m.) of the growing islands is expected to remain unchanged. This is not the case for most of the islands in Fig. 3(c) (with the inset showing a blowup for one of the islands). The islands must be collecting material predominantly from the same direction, since the c.m. is shifted by large distances, comparable to the initial island radius ∼20 nm. The comparison indicates that the amount collected by the islands is not incorporated randomly but in preferred directions and therefore must originate in a correlated and persistent way from far away. A different surprising result not consistent with classical nucleation is that although the islands marked with ← face a large vacant area, (which should be more populated with high density of adatoms), the island growth is paradoxically from almost the opposite island side.

In addition to the preferential directional growth of individual islands, neighboring islands show also correlations in their growth direction [for example, the five islands marked with 1 within the area A outlined in red in Fig. 3(c)

and in white in Figs. 3(a) and 3(b)]. This further supports that the wetting layer must be moving in a correlated way over large distances. The growth of neighboring islands can be used to estimate the distance l_0 over which the material arrives, by checking mass balance, with the main assumption that the amount added to the islands must equal the Pb amount increase within the surrounding area, after the small deposition $\Delta\Theta$. Based on nucleation theory, the latter is the amount collected within the Voronoi area around a given island. Using, for example, the top left island of the five islands, its area increases from 1035 to 2151 nm^2, and it is six layers tall so 7×10^4 Pb atoms are needed for its growth. Its Voronoi area is 4.3×10^4 nm^2 and has only collected 9.6×10^3 atoms after the 0.022 ML deposition. This gives a ratio ∼7 of the number of adatoms added to the available ones (if growth was isotropic), but since growth is directional the ratio is even higher, 14. This large difference indicates that material that was incorporated in the island must originate well outside its Voronoi area.

An average estimate that includes the growth of all the five islands within the outlined area A (of width $w \approx 0.4 \ \mu$m and length $s \approx 0.6 \ \mu$m) gives a quantitative estimate of l_0. The islands cover $a \approx 0.03$ A of A and the needed mass is proportional to the number of islands $n = 5$, their average height $h = 4.6$, and the measured average area increase $\Delta a \approx 1.3a$. The supply to the outlined area A is through the narrow side normal to the growth direction and given by $wl_0\Delta\Theta$. Using $\Delta\Theta = 0.022$ ML (i.e., the increase shown next in red in Fig. 4) $s \approx 0.6 \ \mu$m, and $l_0 = (1.3)(0.03)(hs)/\Delta\Theta$ gives 5 μm, more than 3 times the imaged area.

This simple calculation is only approximate and underestimates l_0 since it was assumed that no other islands are present in the supply area that feeds A. Because other islands must be present, which will be encountered by the moving wetting layer and compete for Pb, l_0 must be larger than 5 μm. Such diffusion distances are very consistent with the typical distances the wetting layer moves in step profile evolution experiments [21]. They are at least ∼50 times larger than ∼0.2 μm the diffusion length from the observed island density, if diffusion was classical and the scaling theory of nucleation is used.

Besides the spatial correlations in the growth of neighboring islands, there are also time correlations in the growth of single islands, which further confirm the nonstochastic motion of the wetting layer from far away. Analysis is shown in Fig. 4 where 4 islands within the area of Fig. 3(c) [marked by letters a, b, c, d] are analyzed to estimate their growth after six incremental depositions. The different colors correspond to amounts 1.220, 1.242 ML (used previously to estimate l_0), 1.270, 1.310 ML [corresponds to Fig. 3(b)], 1.400, 1.490, 1.760 ML. [The island edges for the times shown in Figs. 3(a) and 3(b) are highlighted in white.] The insets show the positions of the c.m. after each
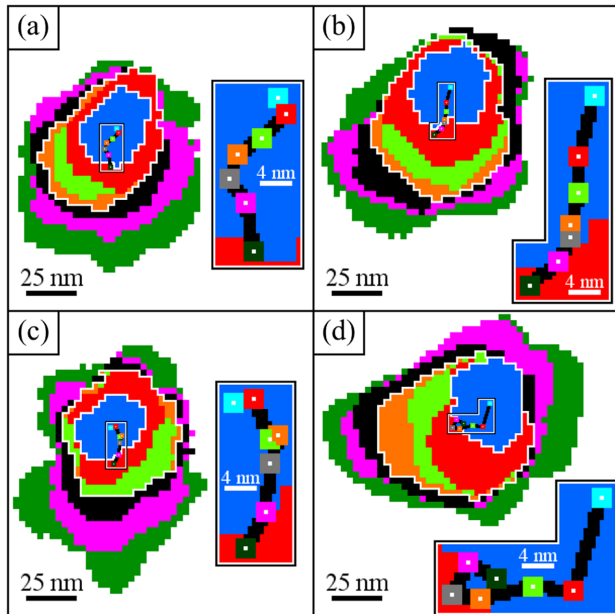
FIG. 4 (color online). The growth of four typical islands marked by letters *a*, *b*, *c*, and *d* in Fig. 3(c) after 6 $\Delta\Theta$ stepwise depositions with 150×150 nm^2 areas and coverages 1.220 ML [blue in Fig. 3(c)], 1.242, 1.270, 1.310 ML [orange in Fig. 3(c)], 1.400, 1.490, 1.760 ML. The edges of the four islands are highlighted in white for the times corresponding to Figs. 3(a) and 3(b). Island *a* in Fig. 3(c) is also identified in Fig. 3(a) by the dashed green line. For most $\Delta\Theta$ depositions the same direction of growth is sustained and the c.m. positions seen in the insets evolve ballistically. These temporal correlations provide further evidence for the collective motion of the wetting layer.

deposition, and not only is there a large shift, but the evolution of the c.m. is almost ballistic. Over the long time of the experiment (~6 h) preferred directions in the island growth are sustained; this is incompatible with random walk diffusion. Islands *a* and *c* grow in SW, island *b* in S and island *d* in W directions. This indicates a "memory" effect of the way material is transferred from the wetting layer to the islands and coherent motion, extending to tens of μms and over hours.

The nucleation experiments reported in this study have extended earlier work [21–26] on Pb/Si(111) with several techniques showing a very unusual type of diffusion, but none of these earlier experiments have examined the explosive nucleation. The first nonclassical fast mass transport observation was made in coarsening experiments, well after nucleation, with surface x-ray scattering. A mixture of islands was initially present with both unstable and stable heights, island stability defined by QSE [22,23]. The decay of the unstable islands was faster by orders of magnitude than what is expected from the known Pb(111) adatom detachment barrier. A more recent experiment with LEEM has shown an even more intriguing result about the wetting layer mobility itself. The refilling of a circular vacant area (a standard profile evolution experiment to measure surface diffusion) was monitored in time over large distances ~0.1 mm [21]. It was found that the refilling not only is superdiffusive, $x \sim t$ (instead of random walk type diffusion $x \sim t^{1/2}$), the refilling profile shows two oppositely moving fronts with the mass generated at the outward front being the mass arriving at the inward refilling one. In a different experiment after C_{60} deposition on the $Pb/Si(111) - \alpha - \sqrt{3} \times \sqrt{3}$ phase, extremely fast transformations were seen, even at 20 K, between different "devil's staircase" (DS) phases as Pb adatoms are "kicked out" [24]. The change between the two DS phases shows fast and error free pattern formation at such low temperatures. A mesoscopic scale refaceting transition observed on a dense DS phase of Pb on the stepped Si(557) surface has unusually high speed at 80 K [25] analogous to the high mass transport observed in the current experiments. Collective diffusion has also been seen in Pb/Ni(111) [26] with similar exceedingly fast motion of the wetting layer when metastable Pb islands decay to their equilibrium shapes. Theoretical work has been carried out to address the question of superdiffusive motion in 2D overlayers but there is still no complete understanding as to its origin [27–30].

In conclusion, the current experiments have shown a novel type of nucleation not expected classically. Once a critical coverage of the Pb/Si wetting layer is reached, $\Theta_c = 1.22$ ML, perfect Pb(111) crystalline multiheight islands emerge explosively. The formation of the islands is very abrupt, despite the low temperatures, and the time of the explosion is less than the STM acquisition time and can be estimated to be a few seconds. Mass transport from the wetting layer to the islands is not via random walk diffusion as in classical nucleation, but through the collective motion of the wetting layer, deduced from the very high transport rate and the strong spatial and temporal correlations in the island growth directions. It is an open problem to search for other systems where this unusual type of nucleation might be present.

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[1] F. F. Abraham, *Homogeneous Nucleation Theory* (Academic Press, New York, 1974).
[2] W. Kurz and D. J. Fisher, *Fundamentals of Solidification*, 4th ed. (Trans Tech Publications, Switzerland, 1998).
[3] *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer (Wiley-VCH, New York, 2005).
[4] J. J. De Yoreo and P. Vekilov in *Biomineralization*, edited by P. M. Dove, J. J. De Yoreo, and S. Weiner (Mineralogical

Society of America, Washington, DC, 2003), Vol. 54, p. 57.

[5] L. Ratke and P. W. Voorhees, *Growth, and Coarsening: Ostwald Ripening in Material Processing* (Springer, New York, 2002).

[6] M. Nishino, C. Enachescu, S. Miyashita, P. A. Rikvold, K. Boukheddaden, and F. Varret, Sci. Rep. **1**, 162 (2011).

[7] R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature (London) **412**, 875 (2001).

[8] Y. Sato, S. Chiang, and N. C. Bartelt, Phys. Rev. Lett. **99**, 096103 (2007).

[9] J. de la Figuera, F. Leonard, N. C. Bartelt, R. Stumpf, and K. F. McCarty, Phys. Rev. Lett. **100**, 186102 (2008).

[10] T. O. Mentes, A. Locatelli, L. Aballe, and E. Bauer, Phys. Rev. Lett. **101**, 085701 (2008).

[11] N. H. P. Nguyen, D. Klotsa, M. Engel, and S. C. Glotzer, Phys. Rev. Lett. **112**, 075701 (2014).

[12] H. J. Zhao, V. R. Misko, and F. M. Peeters, New J. Phys. **14**, 063032 (2012).

[13] J. A. Venables, G. D. T. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984)

[14] H. Brune, Surf. Sci. Rep. **31**, 125 (1998)

[15] J. W. Evans, P. A. Thiel, and M. C. Bartelt, Surf. Sci. Rep. **61**, 1 (2006).

[16] J. Tersoff and F. K. LeGoues, Phys. Rev. Lett. **72**, 3570 (1994).

[17] M. C. Tringides, M. Jalochowski, and E. Bauer, Phys. Today **60**, No. 4, 50 (2007).

[18] R. Feng, E. H. Conrad, C. Kim, P. F. Miceli, and M. C. Tringides, Physica (Amsterdam) **357B**, 175 (2005).

[19] M. Jalochowski and E. Bauer, J. Appl. Phys. **63**, 4501 (1988).

[20] D. Schmicker, T. Hibma, K. A. Edwards, P. B. Howes, J. E. Macdonald, M. A. James, M. Breeman, and G. T. Barkema, J. Phys. Condens. Matter **9**, 969 (1997).

[21] K. L. Man, M. C. Tringides, M. M. T. Loy, and M. S. Altman, Phys. Rev. Lett. **110**, 036104 (2013).

[22] C. A. Jeffrey, E. H. Conrad, R. Feng, M. Hupalo, C. Kim, P. J. Ryan, P. F. Miceli, and M. C. Tringides, Phys. Rev. Lett. **96**, 106105 (2006).

[23] M. Hupalo and M. C. Tringides, Phys. Rev. B **75**, 235443 (2007).

[24] A. V. Matetskiy, L. V. Bondarenko, D. V. Gruznev, A. V. Zotov, A. A. Saranin, and M. C. Tringides, J. Phys. Condens. Matter **25**, 395006 (2013).

[25] M. Czubanowski, A. Schuster, H. Pfnür, and C. Tegenkamp, Phys. Rev. B **77**, 174108 (2008).

[26] T. R. J. Bollmann, R. van Gastel, H. J. W. Zandvliet, and B. Poelsema, Phys. Rev. Lett. **107**, 136103 (2011).

[27] O. U. Uche, D. Perez, A. F. Voter, and J. C. Hamilton, Phys. Rev. Lett. **103**, 046101 (2009).

[28] J. D. Howe, P. Bhopale, Y. Tiwary, and K. A. Fichthorn, Phys. Rev. B **81**, 121410R (2010).

[29] L. Huang, C. Z. Wang, M. Z. Li, and K. M. Ho, Phys. Rev. Lett. **108**, 026101 (2012).

[30] E. Granato, S. C. Ying, K. R. Elder, and T. Ala-Nissila, Phys. Rev. Lett. **111**, 126102 (2013).