

This is the accepted manuscript made available via CHORUS. The article has been published as:

Critical Role of a Buried Interface in the Stranski-Krastanov Growth of Metallic Nanocrystals: Quantum Size Effects in Ag/Si(111)-(7×7)

Yiyao Chen, M. W. Gramlich, S. T. Hayden, and P. F. Miceli

Phys. Rev. Lett. **114**, 035501 — Published 22 January 2015

DOI: [10.1103/PhysRevLett.114.035501](https://doi.org/10.1103/PhysRevLett.114.035501)

The critical role of a buried interface in the Stranski-Krastanov growth of metallic nanocrystals: Quantum Size Effects in Ag/Si(111)7x7

Yiyao Chen, M. W. Gramlich, S. T. Hayden, and P. F. Miceli*

Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA

It is shown that the buried interface between a metallic nanocrystal and its supporting substrate is essential for understanding the stability of the ubiquitous class of nanomaterials that grow on a wetting layer in the Stranski-Krastanov growth mode. Importantly, these new results reveal the broad role played by quantum confinement effects in the growth of thin nanoscale metals. In-situ x-ray scattering experiments on Ag/Si(111)7x7, where the apparent minimum stable thickness of the first two atomic layers on top of the wetting layer has posed a long-standing puzzle, show that the commensurate wetting layer is locally removed by the formation of incommensurate nanoislands, which is unanticipated for the conventional Stranski-Krastanov growth mode. The anomalous lattice expansion that had been previously proposed is not observed and these new results for Ag are explained by electron confinement effects whose manifestation differs from other metals.

PACS numbers: 61.05.cm, 61.46.Hk, 68.35.bd, 68.55.J-

The small size of nanoscale metals can lead to intriguing and unexpected physical behavior that is not observed in larger systems. In particular, the size can dramatically influence the way nanoscale metals are formed, although, such effects are not presently well understood. Because nanoscale metals are widely studied for both fundamental science and technological applications, it is therefore essential to understand the underlying physics that controls their growth and formation. For example, the controlled growth of metals on semiconductors is of high interest for the electrical and optical properties in nanoelectronic, energy conversion and nanolaser applications [1–3]. In thin nanoscale metallic crystals, the quantum confinement of the conduction electrons [4] can change the overall energy landscape to such an extent that the mesoscopic crystal shape is affected [5, 6]. Such “quantum-size-effects” (QSE) [7] are strikingly displayed for Pb nanocrystalline islands grown on the Si(111) surface where, early in the growth, the islands exhibit “magic heights” that differ in multiples of bi-layers [8] and, later in the growth, the nanocrystals exhibit a novel non-classical coarsening behavior towards a single preferred height [9]. In other metals, atomically smooth island surfaces are observed that would be unexpected by conventional growth considerations [10–14]. The oscillating bi-layer stability appears to be uniquely displayed for Pb, although significant attention has been given to Ag where only the first bi-layer or thicker is stable. At present, the effects of QSE on the growth of nanoscale metals is not well established across different metallic systems.

In this Letter it is shown that the stability of Ag nanoislands on Si(111) is related to electron quantum confinement effects and the key insight comes from un-

derstanding the structure of the wetting layer and the buried interface. The newly observed island heights agree with theoretical calculations [15] that include the effects of electron confinement. Moreover, these results have broad significance for the ubiquitous materials systems that grow in the Stranski-Krastanov (SK) mode [16] where islands form after a wetting layer is established. Because most experimental techniques cannot determine the structure of the buried interface, it has always been assumed that the islands grow on top of the wetting layer in a SK growth mode. However, we demonstrate that the commensurate wetting layer dissolves beneath the islands and the islands form an incommensurate interface directly with the substrate. Both results, the dissolving wetting layer in SK growth as well as the demonstration of QSE of Ag islands, are fundamentally important for understanding the growth of metal nanocrystals on supporting substrates.

There have been a number of puzzling results reported for the growth of Ag on Si(111)7x7 where there is extensive interest to understand what role QSE plays in its growth. After the completion of a low-density ($<1/2$ ML) Ag wetting layer that is one atomic layer in thickness and commensurate with the Si(111)7x7, a face-centered-cubic (FCC) Ag bi-layer on top of the wetting layer was believed to be the thinnest stable island height to form as the coverage is increased [13, 17–20]. Most studies show that the bi-layer stability does not repeat with increasing coverage and layer heights greater than a bi-layer occur in *single-layer* increments. The mechanism for the stability of only the first bi-layer has remained as an important question. Unal et al. [20] noticed that their scanning-tunnelling microscopy (STM) measurements and those of other groups *consistently* show an anomalous 12% lattice expansion (relative to bulk Ag) of only the first bi-layer [13, 19, 20]. Consequently, it was proposed that the apparent stability of the first bi-layer could be related to QSE arising from the expanded lattice: because

*e-mail: micelip@missouri.edu

the Fermi level of Ag appears in the gap between bands along $\langle 111 \rangle$, the 12% expansion could strain-shift the Fermi-level into the band for the first bi-layer, thereby enabling its stability, but not for the strain-relieved subsequent layers [20]. The structural and electronic evolution of this mechanism, however, has not been carefully investigated.

The experiment was carried out, *in-situ*, at the Advanced Photon Source on the 6IDC beam line using the resident growth and analysis ultra-high vacuum chamber (base pressure of 1×10^{-10} Torr) that is incorporated into a Psi diffractometer. The photon energy was 16.2 keV. The data are presented in hexagonal reciprocal lattice coordinates $(\text{HKL})_H$, indicated by the H subscript, which are referenced to Si with the following relationship between hexagonal and cubic lattice constants: $a_H = \frac{a}{\sqrt{2}}$ and $c_H = \sqrt{3}a$ where $a=0.5431$ nm and $[003]_H=[111]$ is along the surface normal direction. The Si(111)7x7 surface was prepared by flash-annealing a commercially available 1 mm-thick n-type Si(111) substrate using established methods [21]. Ag was thermally deposited onto the clean Si(111)7x7 surface at the desired temperature, which was determined by a type K thermocouple located on the sample holder. The deposition rate was $\sim 1.1 \pm 0.1$ ML/min, which was established by a quartz crystal oscillator monitor that was calibrated from intensity oscillations during the layer-by-layer homoepitaxial growth of Ag(001). 1 ML is defined as the areal density of Ag(111), 1.38×10^{15} atoms/cm².

The island formation and its relationship to the wetting layer was investigated by measuring both the x-ray specular reflectivity and the crystal truncation rods of FCC Ag. These measurements differ in important ways. The specular reflectivity arises from every atomic layer, independent of the in-plane structure, whereas the crystal truncation rod arises only from atomic layers that have the incommensurate FCC crystal structure of the Ag islands. Fig. 1(a) shows the x-ray specular reflectivity $(\text{Ag}(00L)_H)$ measured for 0.9 ML of deposited Ag, which is approximately one-half ML more coverage than is needed to saturate the wetting layer; thus both wetting layer and islands are present. Qualitatively, the intensity is observed to oscillate along L in a way that is analogous to an optical three-slit interference, indicating the predominance of three atomic layers of Ag. Fig. 1(b) shows a complementary measurement of the incommensurate $\text{Ag}(h,h,L)_H$ crystal truncation rod with $h=1.328$, which also displays the oscillatory intensity that is characteristic of three atomic layers. Both data sets were quantitatively modeled using a distribution of Ag island heights. For the specular reflectivity, the Si(111) substrate, its reconstructed 7x7 surface and a Ag wetting layer were also included. A schematic diagram of the model is shown in Fig. 1, where the p_j are the fraction of the surface occupied by islands having a height, j . The

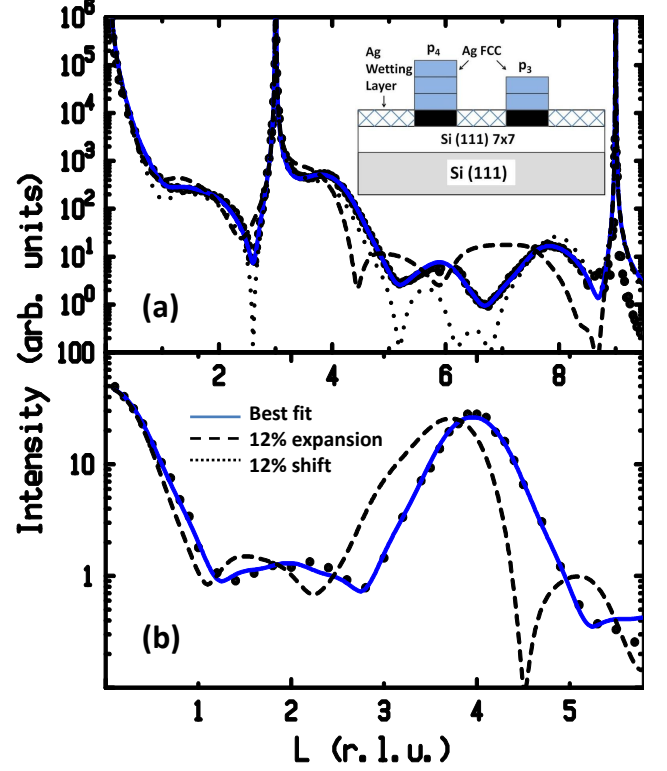


FIG. 1: (a) X-ray specular reflectivity and (b) crystal truncation rod measurements from 0.9 ML of Ag deposited on Si(111)7x7 at 360K. The inset shows a side view of the structural model where the unknown crystal structure of the first atomic layer beneath the islands is indicated in black. Using the bulk Ag lattice constant, the solid curves are the best fit of the model to the data with the island height distribution given in Fig. 2. The dashed curve imposes a 12% lattice expansion on the first bi-layer of Ag. The dotted curve is obtained for islands having the bulk Ag lattice constant but are displaced from the substrate by an amount that is equivalent to a 12% expansion of the first bi-layer.

solid curves in Fig. 1 represent the best fit to the data and a detailed description of the analysis is presented elsewhere [22].

Do the three layers that we observe correspond to a bi-layer of FCC Ag islands on top of the commensurate Ag 7x7 wetting layer, as has been widely assumed in the literature? This question is resolved by comparing the specular reflectivity and truncation rod measurements. Because the truncation rod measurement shows three layers of FCC Ag whereas the reflectivity measurement indicates three *total* layers of Ag, including the wetting layer, it is concluded that the Ag islands have the FCC structure all the way to the substrate. This conclusion is supported quantitatively in Fig. 2 which shows that the island height distribution determined from the two

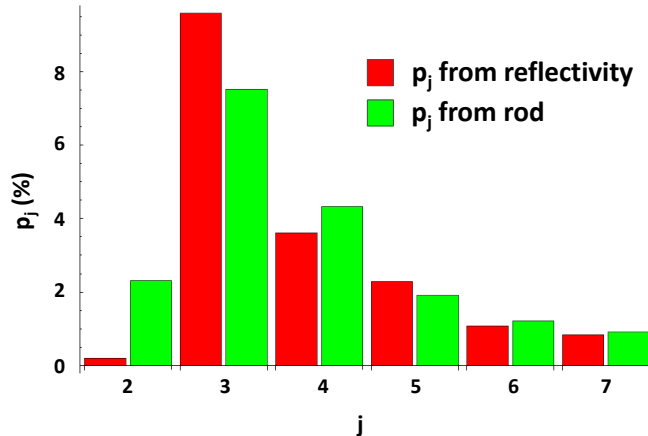


FIG. 2: Comparison of the island height distribution, p_j , obtained from the specular reflectivity and the crystal truncation rod measurements in Fig. 1. The two measurements yield nearly identical height distributions, indicating that the FCC Ag islands extend to the substrate interface rather than reside on top of the wetting layer.

different measurements are nearly identical. Therefore, the Ag nanocrystalline islands do not grow on top of the Ag wetting layer; rather the islands consume the wetting layer beneath them so that all of the FCC Ag islands are in direct contact with the substrate. These results, therefore, reveal that the preferred minimum FCC Ag layer thickness on Si(111)7x7 is a *tri-layer* rather than a bi-layer.

Temperature-dependent measurements of the height distribution, shown in Fig. 3, demonstrate that mobility limits taller islands from forming while the minimum stable height is three layers. Both the island height and the width of the height-distribution are observed to increase with temperature. Therefore, the system tries to reduce the interfacial energy by increasing the island height to the extent permitted by the available mobility. Nevertheless, the inset of Fig. 3 shows that the height distribution is dominated by three-layer islands when only 0.45 ML is deposited, which barely exceeds the wetting layer saturation coverage. Therefore, the *minimum* preferred island height is three layers.

A striking result of these measurements is that the Ag interatomic layer spacing is not expanded, as has been indicated by several STM studies. Instead, the x-ray scattering measurements reveal that the FCC Ag exhibits the ideal bulk Ag distance between all of the atomic layers. As shown in Fig. 1, a 12% lattice expansion for the first two layers does not come close to fitting the data. Since STM measures the distance from the wetting layer to the island tops, we also tried an alternative model where the islands are displaced from the substrate relative to the wetting layer in order to give the equivalent height in-

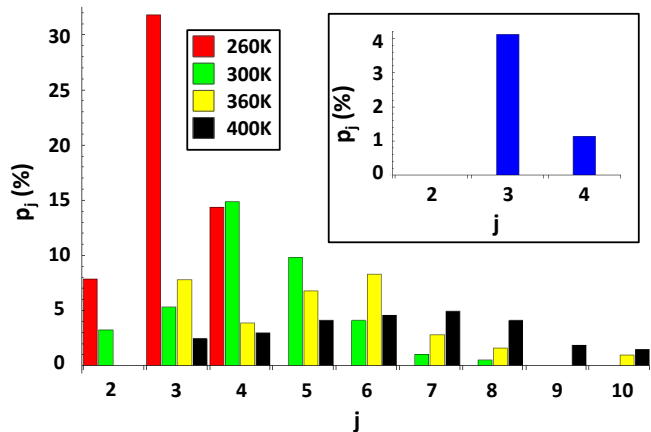


FIG. 3: The island height distribution, p_j , for 1.8 ML of Ag deposited at different temperatures. As the temperature increases, the average island height and the breadth of the distribution increases, which indicates that mobility plays an important role in the observed distributions. The inset shows p_j for 0.45 ML Ag deposited at 300K: even though the coverage barely exceeds the wetting layer saturation (about 5% of the surface is covered by Ag islands), there is a clear preference for three atomic layer islands.

crease without expanding the Ag lattice. This type of interfacial displacement was observed for Pb/Si(111)7x7 [23]. However, that model also fails to fit the reflectivity data. Because x-ray scattering is very sensitive to small changes in distance, the 12% expansion or displacement represents an enormous effect that is not observed in our experiments. We therefore conclude that Ag has the conventional bulk lattice spacing and that the STM measurements are affected by a tunnelling efficiency which prohibits an accurate determination of the distance between the atomic cores.

The FCC Ag islands are also observed to have the conventional Ag lattice constant in the plane of the interface ($\pm 0.1\%$), indicating that the interface with the substrate is insufficient to strain the Ag[24]. The islands are incommensurate with the Si substrate and they exhibit a two-dimensional in-plane orientational disorder over several degrees, as shown in Fig. 4. By comparison, the Ag wetting layer is commensurate and perfectly aligned with the 7x7 reconstruction. However, the absence of strain and the fact that the FCC Ag islands are atomically flat – less than 0.35 Å RMS determined from x-ray reflectivity, consistent with STM[20] – suggests that the orientational fluctuations occur with a relatively weak interaction of the FCC Ag with the substrate. This interaction is certainly much weaker than for the Ag in the commensurate wetting layer.

Without the anomalous lattice expansion, an *oscillating* energy landscape arising from QSE will not explain the minimum nanocrystal thickness of Ag(111) on

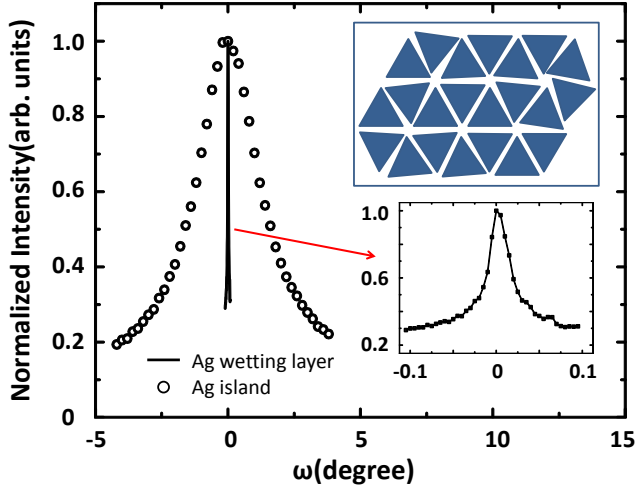


FIG. 4: The large in-plane orientational disorder of the FCC Ag islands is observed by comparing scans performed azimuthally in the surface plane through the $(1.328, 1.328, 0.1)_H$ peak of the FCC Ag islands and the $(8/7, 0, 0.1)_H$ peak of the Ag/Si(111)7x7 wetting layer. The Ag island peak extends more than 3 degrees, which is two orders of magnitude broader than the Ag wetting layer that is commensurate with the Si(111)7x7. The upper inset schematically shows the Ag island mosaicity in the surface plane. The lower inset provides an expanded view of the Ag wetting layer peak.

Si(111)7x7. However, as we will now discuss, our experiments demonstrate that QSE determines the preferred minimum crystal thickness, although, the interface and a different energy landscape must be considered. At the interface there will be equilibrium between the wetting layer and the FCC nanocrystal phases. Because the commensurate wetting layer completes first, its energy/area is significantly lower than for *any* thickness of incommensurate Ag(111). After the wetting layer phase saturates, FCC Ag nanocrystalline islands form upon further coverage, although, not on top of the Ag wetting layer because that interfacial energy is apparently unfavorable as shown by experiment. Instead, the local wetting layer dissolves and it is replaced by incommensurate FCC Ag islands that are in weaker contact with the substrate – there is a coexistence between these two phases.

The important role of quantum confinement is revealed by the excellent agreement between our experimentally observed island height distributions and recent density functional theory (DFT), which includes the effect of electron confinement, performed for free-standing Ag(111) films by Han and Liu [15]. The DFT shows that the energy/area is essentially independent of thickness for layers having 3 ML or more – there is no oscillation with thickness. Including a much lower-energy commensurate wetting layer (not considered in the DFT) will lead to a two-phase coexistence line between the wetting layer and islands having 3 ML or more. At the lowest temperatures, 3 ML will be the thinnest preferred thick-

ness. At higher temperatures, thicker layers will be populated as the mobility increases, which agrees with our experimental observation in Fig. 3. It should be noted that a strong substrate interaction, which is apparently small here, can change the growth behavior. Indeed, if a stronger *commensurate* interaction with the substrate is assumed, DFT [25] shows a significantly different energy/area with thickness of the Ag island.

Therefore, the evidence is now clear that quantum confinement of the conduction electrons influences the growth behavior of *both* Pb(111) and Ag(111): their different growth behaviors (Pb having bi-layer oscillations and Ag exhibiting only the first tri-layer) is a consequence of their different electronic structures. The Pb/Si(111)7x7 system exhibits *persistent* bi-layer growth oscillations because such oscillations are clearly present in the electronic structure of Pb(111) [15]. In the case of Ag(111), however, such oscillations are entirely absent in the thickness-dependent electronic structure [15]. The minimum stable height, which is a Ag tri-layer, is due to QSE of the islands that are in coexistence with the wetting layer.

It is of fundamental interest to understand the behavior of a wetting layer in the growth of dissimilar materials where islands form following the completion of a wetting layer – known as a Stranski-Krastanov growth mode (SK) [16]. Because most measurement techniques cannot see the structure of the buried interface, it has always been *assumed* that the islands grow on top of the wetting layer in the SK growth mode. However, the present x-ray scattering study demonstrates that the portion of the wetting layer below the island is converted to the structure of the metallic island which then has an interface directly with the substrate, without an intervening wetting layer. It is not known how commonly wetting layers are consumed by islands in SK growth because of a lack of in situ experimental studies of buried interfaces. A similar effect was suggested for Pb/Si(111)7x7 [26], although the present measurements are much more direct and conclusive: by measuring both the reflectivity and the truncation rod of FCC Ag for a nearly *monodisperse* island height distribution, the absence of the wetting layer between the metallic island and the substrate could be directly determined. Future studies will be necessary in order to better understand the conditions that lead or do not lead to islands consuming the wetting layer.

In conclusion, we have demonstrated a novel behavior of Stranski-Krastanov (SK) growth which is essential for showing that QSE plays an important role in the stability of Ag nanocrystals. These results have broad general significance for understanding the growth and stability of metallic nanocrystals. Although QSE is strikingly displayed in the growth of Pb nanocrystals through bi-layer oscillations of stability, QSE in Ag is manifested more subtly in terms of a minimum stable thickness. The difference between Pb and Ag derives from their elec-

tronic structure: the electronic energy of Pb oscillates with thickness whereas for Ag the energy is independent of thickness above 3 ML [15]. It is noted that a very recent study of In has shown oscillatory growth, although, there is limited experimental work on this system[27]. Therefore, there is now strong experimental evidence that quantum confinement effects influence the growth and stability of thin metallic nanocrystals, *even when there are no growth oscillations*, as in the case of Ag(111). The unexpected behavior of the SK growth mode, where the wetting layer is locally consumed by the nanocrystals, is a fundamentally important new result for the ubiquitous class of film growth on dissimilar substrate and it requires further investigation. It is essential to understand both the modified SK growth and quantum confinement effects in order to manipulate nanoscale materials at surfaces.

Support from the National Science Foundation under grants DMR-0706278 and DGE-1069091 is gratefully acknowledged. The Advanced Photon Source at Argonne National Laboratory is supported by the US-DOE under Contract No. W-31-109-Eng-38. We are also grateful to M. C. Tringides and S. Satpathy for helpful discussions.

-
- [1] D. D. Awschalom and M. E. Flatte, *Nature Phys.* **3**, 153 (2007).
 - [2] P. Fan, U. K. Chettiar, L. Cao, F. Afshinmanesh, N. Engheta, and M. L. Brongersma, *Nature Photon.* **6**, 380 (2012).
 - [3] Y.-J. Lu, J. Kim, H.-Y. Chen, C. Wu, N. Dabidian, C. E. Sanders, C.-Y. Wang, M.-Y. Lu, B.-H. Li, X. Qiu, W.-H. Chang, L.-J. Chen, G. Shvets, C.-K. Shih, and S. Gwo, *Science* **337**, 450 (2012).
 - [4] T. C. Chiang, *Surf. Sci. Rep.* **39**, 181 (2000).
 - [5] M. Ozer, C.-Z. Wang, Z. Zhang, and H. Weitering, *J. Low Temp. Phys.* **157**, 221 (2009).
 - [6] W. B. Su, C. S. Chang, and T. T. Tien, *J. Phys. D* **43**, 013001 (2010).
 - [7] F. K. Schulte, *Surf. Sci.* **55**, 427 (1976).
 - [8] K. Budde, E. Abram, V. Yeh, and M. C. Tringides, *Phys. Rev. B* **61**, R10602 (2000).
 - [9] 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).
 - [10] A. R. Smith, K.-J. Chao, Q. Niu, and C.-K. Shih, *Science* **273**, 226 (1996).
 - [11] Z. Zhang, Q. Niu, and C.-K. Shih, *Phys. Rev. Lett.* **80**, 5381 (1998).
 - [12] L. Huang, S. Jay Chey, and J. H. Weaver, *Surf. Sci.* **416**, L1101 (1998).
 - [13] L. Gavioli, K. R. Kimberlin, M. C. Tringides, J. F. Wendelken, and Z. Zhang, *Phys. Rev. Lett.* **82**, 129 (1999).
 - [14] D.-A. Luh, T. Miller, J. J. Paggel, M. Y. Chou, and T.-C. Chiang, *Science* **292**, 1131 (2001).
 - [15] Y. Han and D.-J. Liu, *Phys. Rev. B* **80**, 155404 (2009).
 - [16] J. A. Venables, *Introduction to Surface and Thin Film Process* (Cambridge University Press, 2000).
 - [17] P. Sobotik, I. Ost'adal, J. Myslivecek, T. Jarolimek, and F. Lavicky, *Surf. Sci.* **482-485**, 797 (2001).
 - [18] W. B. Su, H. Y. Lin, Y. P. Chiu, H. T. Shih, T. Y. Fu, Y. W. Chen, C. S. Chang, and T. T. Tsong, *Phys. Rev. B* **71**, 073304 (2005).
 - [19] D. K. Goswami, K. Bhattacharjee, B. Satpati, S. Roy, P. V. Satyam, and B. N. Dev, *Surf. Sci.* **601**, 603 (2007).
 - [20] B. Unal, A. Belianinov, P. A. Thiel, and M. C. Tringides, *Phys. Rev. B* **81**, 085411 (2010).
 - [21] M. W. Gramlich, S. T. Hayden, Y. Chen, C. Kim, E. H. Conrad, M. C. Tringides, and P. F. Miceli, *Phys. Rev. B* **84**, 075433 (2011).
 - [22] Y. Chen, M. W. Gramlich, S. T. Hayden, and P. F. Miceli, manuscript in preparation.
 - [23] C. A. Jeffrey, R. Feng, E. H. Conrad, P. F. Miceli, C. Kim, M. Hupalo, M. C. Tringides, and P. J. Ryan, *Superlattices Microst.* **41**, 168 (2007).
 - [24] The current experiments consist of uncoalesced nanoscale Ag islands. Thicker Ag films can exhibit strain under certain conditions; see: G. Neuhold and K. Horn, *Phys. Rev. Lett.* **78**, 1327 (1997); C. Kim, R. Feng, E. H. Conrad, and P. F. Miceli, *Appl. Phys. Lett.* **91**, 093131 (2007).
 - [25] D. Shao, X. Liu, N. Lu, C. Z. Wang, K.-M. Ho, M. C. Tringides, and P. A. Thiel, *Surf. Sci.* **606**, 1871 (2012).
 - [26] R. Feng, E. H. Conrad, M. C. Tringides, C. Kim, and P. F. Miceli, *Appl. Phys. Lett.* **85**, 3866 (2004).
 - [27] A. Gray, Y. Liu, H. Hong, and T. C. Chiang, *Phys. Rev. B* **87**, 195415 (2013).