PHYSICAL REVIEW B **93**, 075443 (2016)

Optical and structural properties of the pentacene/quartz (0001) interface

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(Received 31 December 2015; revised manuscript received 3 February 2016; published 29 February 2016)

Here we investigate the growth of the pentacene thin film on the quartz (0001) surface. The evolution of the optical properties of the pentacene thin film has been monitored *in situ* by optical spectroscopy and the thin-film morphology was investigated *ex situ* by atomic force spectroscopy. We find that (001)-oriented thin-film phase pentacene crystallites grow on a one-monolayer-thick interfacial layer. The optical and structural properties of the first monolayer determined *in situ* and *ex situ*, respectively, differ substantially from those of the multilayers. Most importantly, the distinct optical properties of the first monolayer are preserved when the interface becomes buried during the subsequent pentacene thin-film formation.

DOI: 10.1103/PhysRevB.93.075443

I. INTRODUCTION

The formation of an interfacial layer and its possible modification upon subsequent multilayer growth is important for the understanding of the performance of organic thin-film devices [1–4]. It has been recognized that the organic/organic and organic/inorganic interfaces in organic electronic devices play a key role regarding device functionality and efficiency [1–3]. However, characterization of these interfaces is quite challenging because the interfacial layer generally involves a few molecular layers only and thus requires analytical methods with very high sensitivity [1–3]. Furthermore, the interfacial layers are usually buried under thick films constituting molecules of the same species and, consequently, are very hard to discriminate. On the other hand, the optical properties of organic molecular layers at the interface exhibit distinct optical properties [5–9] which depend on the molecular environment as well as on the vertical interaction with the substrate. In fact, the electrostatic interaction generally introduces a spectral shift in analogy to a solvent shift, whereas the resonant molecular interaction may introduce excitonic effects including Davydov splitting [10,11]. Consequently, optical spectroscopy provides a sensitive probe to the interfacial properties, including molecular orientation, conformation, and local environment [5–9,11]. Furthermore, photons in the visible and near-ultraviolet range can penetrate rather deeply into the organic film without introducing significant damage. Therefore, optical spectroscopy constitutes a suitable method to probe buried organic interfacial layers [11].

The deposition of pentacene molecules on SiO_2 substrates has attracted numerous attention and is regarded as a prototype system for the investigation of organic thin-film growth. Accordingly, a strong influence of the surface condition on the growth of pentacene thin films has been indicated [12–14]. However, most of the published results up to now were about the growth of pentacene on amorphous SiO_2 layers formed either natively or thermally on silicon substrates. It is thus interesting to investigate the pentacene growth on single-crystal quartz substrate in order to understand the influence of the substrate crystallinity on the growth and the interface structure.

In this study, we have applied a very sensitive optical spectroscopy method, namely, differential reflectance spectroscopy (DRS) [15], to investigate *in situ* the growth of pentacene thin films on a quartz (0001) substrate. By analyzing the spectral evolution of the DR signal during growth, it becomes clear that pentacene crystallizes into the (001)-oriented thin-film phase [16–18] on top of a one-monolayer-thick interfacial layer. The first monolayer exhibits an optical fingerprint which differs from that of the multilayer regarding the spectral position and the size of the Davydov splitting. The latter can be explained by a different molecular arrangement in the first pentacene monolayer. Most importantly, the spectral evolution reveals the preservation of the optical and, thus, the structural properties of the first monolayer when it becomes buried as an interfacial layer. This conclusion, deduced from optical spectroscopy, is corroborated by the analysis of the surface morphology using atomic force microscopy (AFM).

II. EXPERIMENT

The pentacene layers were deposited from a quartz effusion cell in a vacuum chamber with a base pressure lower than 3×10^{-7} mbar. The evaporation rate was about 0.25 Å/min

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as monitored by a quartz microbalance located next to the sample. Single-crystalline quartz with a (0001) orientation was used as the substrate. Epi-ready substrates (SurfaceNet GmbH) were introduced into the vacuum chamber directly without further cleaning. The substrates were then maintained in the vacuum chamber for more than 12 h before pentacene deposition in order to desorb the water and other gas molecules on the surface. The back side of the substrate is rough and thus does not affect the reflected signal. During deposition the quartz substrate was kept at room temperature. The evolution of the optical properties of pentacene thin films during growth was monitored with a home-built differential reflectance spectrometer. The DRS setup was operated in a normal incidence geometry, using a super-quiet Xe lamp (Hamamatsu) as light source and a QE65000 spectrometer (Ocean Optics) with a back-thinned CCD array as the detector. With an integration interval of a few seconds, a spectrum with high signal-to-noise ratio over a spectral range from 1.5 eV to 3.5 eV can be obtained. The differential reflectance spectra are obtained from the measured reflectivities via [15]

$$\frac{\Delta R}{R} = \frac{R(d) - R_0}{R_0}, \qquad (1)$$

where R_0 and $R(d)$ denote the reflectance of the bare surface and the surface covered by an adlayer with a nominal thickness d, respectively. The so-obtained DR signal $\Delta R/R$ thus represents the change of the optical reflectance relative to the bare substrate surface as a function of the nominal film thickness d. The morphology of the grown pentacene thin films was characterized *ex situ* using atomic force microscopy (Dimension 3100, Bruker). More specifically, the tapping mode controlled by amplitude feedback using a very soft cantilever (MikroMasch, force constant around 0.5 N/m) was employed.

III. RESULTS AND DISCUSSION

A. Evolution of the optical properties during growth

The two-dimensional (2D) map in Fig. 1(A) shows the variation of the DR spectra as a function of deposition time. The appearance and evolution of the DR features with increasing deposition time can be attributed directly to the optical absorption of the pentacene layer grown on the transparent quartz substrate. From the selected spectra in Fig. 1(B), it can be recognized that the spectral line shape is very similar over the entire growth period. However, a systematic redshift with increasing film thickness can be noticed, in particular, for the two lowest energy features a and b. The spectral shift is better manifested in Fig. 1(C) where the evolution of the position of the maximum of the DR peak a, corresponding to the lowest electronic transition, is plotted. Based on the character of the spectral shift, the growth can be divided into two stages. During the first stage, the spectral shift is relatively slow, whereas the second stage features a rather fast redshift at the beginning, which gradually slows down with increasing layer thickness. We assign the first stage to the growth of the first monolayer of (upright standing) pentacene molecules. The monotonic and smooth evolution of the spectral shift (instead of a stepwise evolution) during the second stage of growth can be attributed to a three-dimensional (3D) growth mode. This conclusion is corroborated by *ex situ* AFM measurements (see Fig. 4), which will be discussed in detail later.

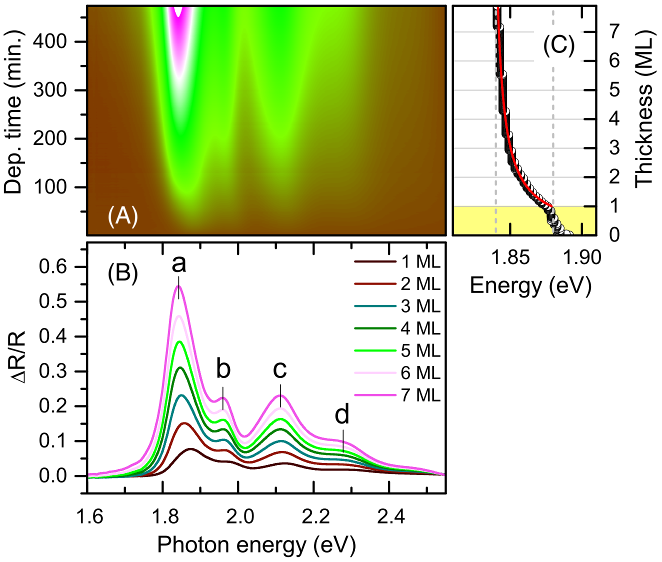

FIG. 1. (A) 2D map representing the DR spectra recorded as a function of deposition time during the growth of pentacene on the quartz (0001) surface at room temperature. (B) DR spectra for several selected film thicknesses. The four bands developing during the growth are marked by a, b, c, and d, respectively. (C) Energy position of the peak maximum associated with the lowest electronic transition (a) as a function of the nominal film thickness. The first growth stage is marked in yellow.

Considering the spectral redshift beyond the first monolayer, the energetic position E of the lowest electronic transition can be fitted nicely using [19]

$$E = E_b + \Delta E \frac{d_{it}}{d}, \qquad (2)$$

where E_b is the absorption energy of bulk pentacene, ΔE represents the energy difference between the optical absorption of the interfacial layer and the bulk, and d_{it} and d are the nominal thicknesses of the interfacial layer and of the thin film in monolayer units (ML), respectively. Equation (2) has been also used to model the growth of pentacene and perfluoropentacene thin films on native oxide covered Si and perylenetetracarboxylic dianhydride (PTCDA) on mica [5,6]. The best fit with fitting parameters $E_b = 1.84$ eV, $\Delta E = 40$ meV, and $d_{it} = 1$ [red line in Fig. 1(C)] accurately reproduces the experimental data. This result illustrates that the DR spectrum is a superposition of two contributions, namely, the absorption of the interfacial layer (dominantly the first monolayer) and the bulk, respectively. The lowest electronic transition energy E approaches the bulk value E_b with increasing film thickness due to the reduced weighting of the interfacial contribution. It is worth emphasizing that the absolute spectral contribution from the interface stays unchanged during subsequent deposition. This can be seen more clearly in Fig. 2 where the difference between two subsequent $\Delta R/R$ spectra in Fig. 1(C) is plotted. These difference spectra [$\Delta(\Delta R/R)$] thus reflect the incremental changes of the optical properties of the pentacene film with the deposition of each monolayer. Indeed, all the $\Delta(\Delta R/R)$, from the second monolayer on, are almost identical to the

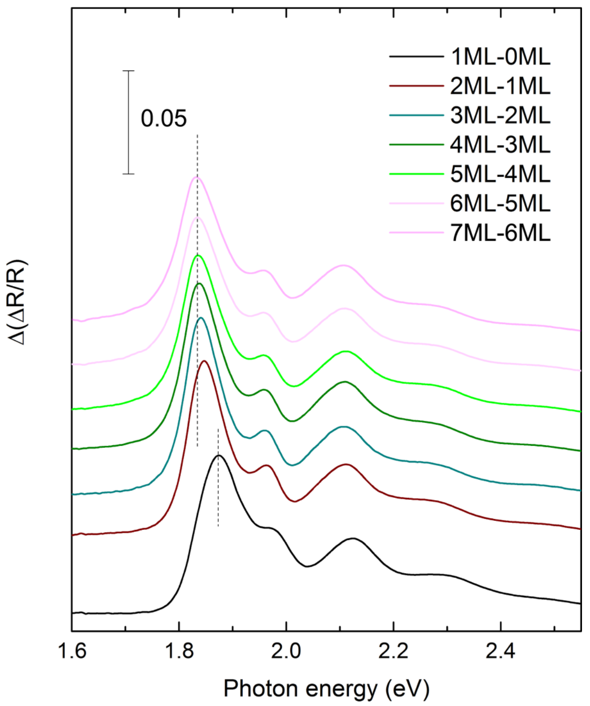

FIG. 2. Difference between subsequent $\Delta R/R$ spectra in Fig. 1(C) revealing the incremental changes of the optical properties for each deposited monolayer.

characteristic spectrum of the bulk. Furthermore, there is no hint of any variation of the spectral contribution of the first ML upon subsequent deposition. For instance, if the spectral feature of the first monolayer would shift, a differential shape would occur in the corresponding $\Delta(\Delta R/R)$ spectrum. Consequently, the important conclusion one can draw from these data is that the optical properties of the first monolayer are not modified upon being buried by the subsequently deposited multilayer.

Since quartz is transparent in the spectral range of interest for the current study, the imaginary part of the dielectric function ε_2 of the thin pentacene layers can be deduced directly from the DR spectra presented in Fig. 1 using the McIntyre approximation [20,21]. Figure 3 depicts the so-determined ε_2 of pentacene thin films with a thickness of 1 ML and 7 ML, respectively. For the 7-ML-thick film, ε_2 exhibits the same spectral characteristics as for the first monolayer but is redshifted to lower energies. Actually, the ε_2 of the 7-ML-thick film closely matches the spectrum of bulk pentacene condensed in the thin-film phase [22–24]. Due to the resonant intermolecular interaction and the existence of two translationally nonequivalent molecules in the unit cell, the lowest electronic transition splits into two bands in the crystal due to the so-called Davydov splitting [10]. The first two absorption peaks indicated by a and b in Fig. 3 can thus be assigned to the lower and the upper Davydov components of the charge-transfer exciton, respectively [24]. Features c and d at higher energies are attributed to the highest occupied and lowest unoccupied molecular orbital band gap and its first vibronic replica, respectively [22–24]. Accompanying the redshift of the lower Davydov component a discussed in Fig. 1, the upper component b shifts in the same place, indicating the same excitonic nature of this transition. The presence of a Davydov splitting from the very beginning of the growth suggests that the standing molecules in the 2D monolayer islands are already packed in a herringbone configuration. Another interesting observation is that the Davydov splitting, i.e., the energy difference between a and b, is about 25% smaller in the first monolayer as compared to the 7-ML-thick film (90 ± 10 meV vs 120 ± 10 meV, respectively). In fact, the size of the Davydov splitting is determined by the strength of the resonant coupling between two pentacene molecules in the unit cell and depends on the degree of their overlap [10]. The different splitting, therefore, implies that the molecular interaction in the first monolayer differs from that in the multilayer. In fact, an increase of the Davydov splitting of pentacene thin films due to thermal contraction at low temperature has been reported by Faltermeier *et al.* [22]. In a recent study, Helzel *et al.* have revealed a change of the Davydov splitting of the interfacial pentacene layer due to the strain induced by the ZnO substrate at low temperature [23]. The distinct optical properties for the first monolayer can thus be attributed to the presence of the interface. By establishing the interface with the foreign substrate, the organic molecules experience a different environment from those located in the multilayer regarding dielectric screening, adhesion, etc. These interfacial effects thus result in distinctive physical properties of the interfacial layer regarding its crystalline structure, and electronic and optical properties. The thickness of the interfacial layer could be 1 ML or even several monolayers thick depending on the strength and type of the interaction at the interface. For the current case of pentacene grown on quartz (0001), the fact that the spectral shift can be fitted nicely using Eq. (2) with $d_{it} = 1$ reveals that the interfacial layer has a thickness of a single monolayer and that its optical properties are not modified upon subsequent growth of multilayers above it.

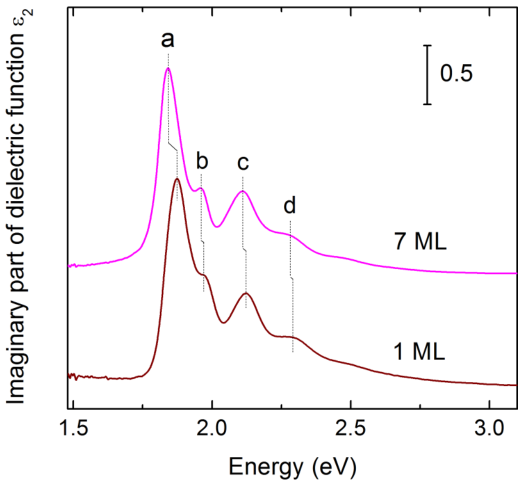

FIG. 3. Imaginary part of the dielectric function (ε_2) of pentacene thin films with a nominal thickness of 1 ML and 7 ML, respectively, deduced from the DR spectra plotted in Fig. 1. The bands a and b are corresponding to the lower and the upper Davydov components, respectively. The features c and d are assigned to the absorption due to the electronic transition from the highest occupied to the lowest unoccupied molecular orbital and its first vibronic replica, respectively.

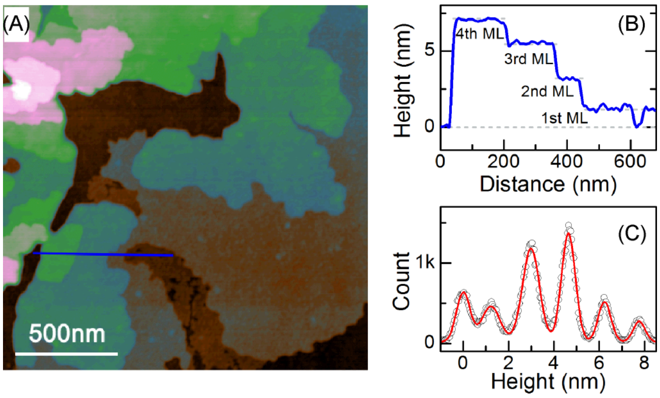

FIG. 4. (A) AFM image measured on the quartz (0001) substrate covered by a pentacene layer with a nominal thickness of 3 ML. (B) Height profile recorded along the blue line indicated in (A). (C) Height histogram obtained from a 2 μm × 2 μm AFM image recorded from the same sample (open circles) together with a fit to Gaussian curves (red solid line).

B. Ex situ characterization of the film morphology

In order to evaluate the morphology of the pentacene thin films, AFM measurements in tapping mode were carried out *ex situ* after sample transfer to air. The morphology of a nominally 3-ML-thick film is depicted in Fig. 4(A). The AFM image corroborates the growth of 3D islands on top of a wetting layer, as inferred from the DRS experiments. The height profile along the blue line in the image is plotted in Fig. 4(B). Figure 4(C) shows the height histogram calculated from a 4-μm^2 image recorded from the same sample. Fitting the height histogram with Gaussian functions, the level of each terrace can be determined. The height difference between subsequent levels is about 1.58 nm, indicating that the layers comprise (nearly upright) standing pentacene molecules. Indeed, the interlayer distances between (001) planes $h_{(001)}$ for the thin-film phase, the single-crystal phase, and the bulk phase of pentacene have been determined by x-ray diffraction (XRD) to be ~1.55 nm [16–18], ~1.41 nm [25–27], and ~1.45 nm [25,28], respectively. Among these three different phases, $h_{(001)}$ is largest for the thin-film phase, corresponding to a configuration with almost perfectly upright standing molecules. From the measured dielectric function and the layer heights, we conclude that the pentacene multilayer beyond the first monolayer consists of crystallites of the thin-film phase with the (001) plane parallel to the substrate. This crystalline orientation is most generally observed for pentacene thin films grown on weakly interacting dielectric substrates, due to the fact that the smallest surface energy is obtained for the (001) plane. With a closer look at Figs. 4(B) and 4(C), a smaller height (by about 5%) can be discerned for the first monolayer as compared to the layers above. Consequently, it is reasonable to believe that the molecules in the first monolayer pack in a slightly different configuration. In fact, the smaller layer thickness of the monolayer indicates a larger tilt angle of the long molecular axis with respect to the surface normal. A similar situation has been observed by Hlawacek *et al.* for the growth of parasexiphenyl molecules on mica [29]. This geometry apparently leads to a lower packing density as well as a reduced π-π overlap between neighboring molecules. Ultimately, a weaker lateral interaction between molecules can be expected. This is consistent with the smaller Davydov splitting observed for the first monolayer. On the other hand, possible variation of the thin-film morphology upon exposing the sample to air cannot be excluded completely. Consequently, a direct correlation between the characteristic optical and structural properties measured *in situ* and *ex situ*, respectively, should be considered with caution. Furthermore, it is interesting to note that the height of the first pentacene monolayer grown on amorphous SiO_2 substrate is larger than the interlayer distance between the (001) plane $h_{(001)}$ for the thin-film phase due to a smaller tilt angle of the long molecular axis with respect to the surface normal [30–32]. This structural distinction between pentacene monolayers grown on the quartz and the amorphous SiO_2 substrates indicates the influence of the substrate crystallinity to the growth and ultimately the interface structure.

IV. CONCLUSION

In conclusion, we have investigated the growth of pentacene thin films on the quartz (0001) surface at room temperature. The pentacene multilayers crystallize in the thin-film phase forming (001)-oriented 3D islands of nearly upright standing molecules. Furthermore, the reflectance of the pentacene layer shows a characteristic evolution in accordance with the transition from the monolayer towards the 3D bulk phase, demonstrating the sensitive dependence of the optical properties on the crystalline structure and the dielectric environment. Most importantly, the quantitative analysis of the optical spectroscopy data reveals that the optical properties of the buried interfacial layer are preserved upon subsequent thin-film growth. This observation also suggests the conservation of the corresponding molecular configuration. On the other hand, according to the *ex situ* AFM measurement, the first monolayer at the interface deviates from the thin-film phase structure by a larger tilt of the long molecular axis with respect to the surface normal. This is in strong contrast with the pentacene monolayer grown on amorphous SiO_2 substrates.

ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (Grant No. 2012CB937500), the National Natural Science Foundation of China (Grant No. 61008028), the Foundation for the Author of National Excellent Doctoral Dissertation of China (Grant No. 201140), 111 Project of China (Grant No. B07014), the Austrian Science Fund FWF (P25377), and Eurasia Pacific Uninet.

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[1] N. Koch, ChemPhysChem **8**, 1438 (2007).
[2] F. Dinelli, M. Murgia, P. Levy, M. Cavallini, F. Biscarini, and D. M. de Leeuw, Phys. Rev. Lett. **92**, 116802 (2004).
[3] A. Shehu, S. D. Quiroga, P. D'Angelo, C. Albonetti, F. Borgatti, M. Murgia, A. Scorzoni, P. Stoliar, and F. Biscarini, Phys. Rev. Lett. **104**, 246602 (2010).

[4] T. Hosokai, A. Hinderhofer, F. Bussolotti, K. Yonezawa, C. Lorch, A. Vorobiev, Y. Hasegawa, Y. Yamada, Y. Kubozoro, A. Gerlach, S. Kera, F. Schreiber, and N. Ueno, J. Phys. Chem. C **119**, 29027 (2015).

[5] H. Proehl, T. Dienel, R. Nitsche, and T. Fritz, Phys. Rev. Lett. **93**, 097403 (2004).

[6] U. Heinemeyer, K. Broch, A. Hinderhofer, M. Kytka, R. Scholz, A. Gerlach, and F. Schreiber, Phys. Rev. Lett. **104**, 257401 (2010).

[7] C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, and A. Borghesi, Org. Electron. **5**, 73 (2004).

[8] E. Dell'Orto, L. Raimondo, A. Sassella, and A. Abbotto, J. Mater. Chem. **22**, 11304 (2012).

[9] L. D. Sun, J. Gall, G. Weidlinger, C. Y. Liu, M. Denk, and P. Zeppenfeld, Phys. Rev. Lett. **110**, 106101 (2013).

[10] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, New York, 1999).

[11] L. D. Sun, S. Berkebile, G. Weidlinger, M. Denk, R. Denk, M. Hohage, G. Koller, F. P. Netzer, M. G. Ramsey, and P. Zeppenfeld, Phys. Chem. Chem. Phys. **14**, 13651 (2012).

[12] A. C. Mayer, R. Ruiz, R. L. Headrick, A. Kazimirov, and G. G. Malliaras, Org. Electron. **5**, 257 (2004).

[13] S. E. Fritz, T. W. Kelley, and C. D. Frisbie, J. Phys. Chem. B **109**, 10574 (2005).

[14] H. Peisert, T. Schwieger, J. M. Auerhammer, M. Knupfer, M. S. Golden, J. Fink, P. R. Bressler, and M. Mast, J. Appl. Phys. **90**, 466 (2001).

[15] R. Forker and T. Fritz, Phys. Chem. Chem. Phys. **11**, 2142 (2009).

[16] D. Nabok, P. Puschnig, C. Ambrosch-Draxl, O. Werzer, R. Resel, and Detlef-M. Smilgies, Phys. Rev. B **76**, 235322 (2007).

[17] S. Schiefer, M. Huth, A. Dobrinevski, and B. Nickel, J. Am. Chem. Soc. **129**, 10316 (2007).

[18] H. Yoshida, K. Inaba, and N. Sato, Appl. Phys. Lett. **90**, 181930 (2007).

[19] V. M. Agranovich, R. D. Atanasov, and G. F. Bassani, Chem. Phys. Lett. **199**, 621 (1992).

[20] J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **24**, 417 (1971).

[21] R. Forker, M. Gruenewald, and T. Fritz, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **108**, 34 (2012).

[22] D. Faltermeier, B. Gompf, M. Dressel, A. K. Tripathi, and J. Pflaum, Phys. Rev. B **74**, 125416 (2006).

[23] J. Helzel, S. Jankowski, M. El. Helou, G. Witte, and W. Heimbrodt, Appl. Phys. Lett. **99**, 211102 (2011).

[24] M. L. Tiago, J. E. Northrup, and S. G. Louie, Phys. Rev. B **67**, 115212 (2003).

[25] T. Siegrist, C. Besnard, S. Haas, M. Schiltz, P. Pattison, D. Chernyshov, B. Batlogg, and C. Kloc, Adv. Mater. **19**, 2079 (2007).

[26] D. Holmes, S. Kumaraswamy, A. J. Matzger, and K. P. C. Vollhardt, Chem. Eur. J. **5**, 3399 (1999).

[27] T. Siegrist, C. Kloc, J. H. Schön, B. Batlogg, R. C. Haddon, S. Berg, and G. A. Thomas, Angew. Chem., Int. Ed. **40**, 1732 (2001).

[28] R. B. Campbell, J. M. Robertson, and J. Trotter, Acta Crystallogr. **15**, 289 (1962).

[29] G. Hlawacek, P. Puschnig, P. Frank, A. Winkler, C. Ambrosch-Draxl, and C. Teichert, Science **321**, 108 (2008).

[30] R. Ruiz, B. Nickel, N. Koch, L. C. Feldman, R. F. Haglund, A. Kahn, and G. Scoles, Phys. Rev. B **67**, 125406 (2003).

[31] G. Yoshikawa, T. Miyadera, R. Onoki, K. Ueno, I. Nakai, S. Entani, S. Ikeda, D. Guo, M. Kiguchi, H. Kondoh, T. Ohta, and K. Saiki, Surf. Sci. **600**, 2518 (2006).

[32] S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward, and M. F. Toney, J. Am. Chem. Soc. **126**, 4084 (2004).