Luminescence quenching of tetracene films adsorbed on an ultrathin alumina AlO$_x$ layer on Ni$_3$Al(111)

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We have investigated the luminescence quenching of the fluorescent aromatic molecule tetracene (Tc) adsorbed on an ultrathin film of alumina on a Ni$_3$Al(111) substrate. The alumina film (thickness ~5 Å) was grown by heating a Ni$_3$Al(111) crystal under an oxygen atmosphere. Directly after deposition of Tc molecules at low temperatures (45 K), the Tc films are disordered and *no* luminescence can be detected. We explain this by charge transfer to the Ni$_3$Al(111) substrate from mainly *flat-lying* Tc molecules across the alumina film. After an additional annealing cycle at 240 K, we observe a significant luminescence signal for films with nominal film thickness down to submonolayers. Low energy electron diffraction measurements reveal that the annealing cycle leads to formation of (001) oriented Tc crystallites with Tc molecules *standing nearly perpendicular* to the surface. We hence propose that the luminescence quenching by charge transfer is inhibited for the annealed Tc films due to the different molecule orientation and film morphology. In control experiments performed on the sapphire (0001) surface, we find a very similar behavior, except that we can detect a very low luminescence signal already for the as grown Tc films. However, the luminescence yield is very small, likely due to structural disorder.

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I. INTRODUCTION

Fluorescence processes of aromatic molecules on *well-defined* single crystal surfaces have become of interest under several aspects recently (see, e.g., Refs. [1–3]). One of these is the use of the fluorescence signal, exited by an optical far-or near-field or by a tunneling current to the substrate from a scanning tunneling microscope (STM) tip,[4–7] to obtain information about molecules on surfaces. This information may concern the adsorption state of the molecules on the surface itself or its site within small molecular agglomerates such as islands, clusters, or thin films on the surface. In addition, there may be a possibility to use the fluorescence signal as a tool to study kinetic processes, e.g., diffusion of molecules on surfaces. Evidently, such experiments require that the molecules on the surface fluoresce and that the fluorescence process is not totally quenched by energy or charge transfer to the underlying substrate. Hence, an important aspect is the understanding of quenching processes, i.e., nonradiative decay mechanisms, of the molecular fluorescence on surfaces itself.[2,3,8]

Several examples of thin films of fluorescent aromatic molecules on well-defined single crystal surfaces were studied in the past.[1,9–12] A large number of these experiments have investigated the influence of the structure and morphology of the films on the fluorescence spectra.[9–12] However, on metal surfaces, quenching processes appear to limit the use of the fluorescence technique for the first two layers. In particular, for the Ag(111) surface we found from photoluminescence (PL) experiments that, in addition to the classical *energy transfer* to the image dipole in the metal,[13] there exists an ultrafast quenching process for the first two layers of molecules at the film/substrate interface.[2] This result was obtained for films of quaterthiophene,[2] 3,4,9,10-perylenetetra-carboxylicacid-dianhydride (PTCDA),[2] and recently also for tetracene[14] on the Ag(111) surface. In all these cases, the molecules are adsorbed in a more or less planar geometry

due to the chemical bonding of the molecules to the metal substrate via the π electron system. As a consequence, inter-mixed states of the π electron system and the Ag(111) substrate exist, which can easily permit an ultrafast *charge transfer* to the substrate after an optical excitation and lead to a nonradiative deexcitation, i.e., quenching of the fluorescence. Although the number of studied examples is still limited, we propose that this mechanism is of some general validity for aromatic molecules adsorbed on metal surfaces, whenever there exists a sufficient overlap of the π electron system, which is responsible for the fluorescence properties, and the metal substrate states. We note that the luminescence quenching for the first two layers was also found for films of porphorines on the Au(111) surface exited by a tunneling current from a STM tip (STM excitation).[6]

The number of photoluminescence experiments performed for molecules on *well-defined* surfaces of wide band gap materials or insulators is very small so far. For quater-thiophene (4T) on ZnSe(100) we could not observe luminescence, unless the layers were annealed and presumably small 4T clusters had formed.[3] Photoluminescence of PTCDA monolayers on mica[15] and quartz glass were reported.[1] In addition, fluorescence spectra were obtained for porphorines adsorbed on a thin alumina film on NiAl(110) (Ref. [5]) or on the Cu(100) surface,[4] when these molecules were excited by STM. Notably, bulky tert-butyl groups were attached to these porphorines, which separate the π system from the metal surface. In this aspect, theses molecules hence differ considerably from the here-investigated planar tetracene, which allows us to bring the π system closer to the surface. In addition, fluorescence and phosphorescence were recently observed for C_{60} on thin NaCl films at low temperatures under the STM tip.[7] Finally we note that a number of investigations on the fluorescence, partly time resolved but without further structural control, were performed for thin films of dye molecules (e.g., rhodamine) adsorbed on insulators

from solution (see, e.g., Refs. 16–19). In particular, vapor deposited films of tetracene (50 Å nominal thickness) were studied on LiF spacer layers with thicknesses down to 10 Å.[20]

In the present manuscript, we report an investigation on tetracene (Tc), adsorbed on an ultrathin film of alumina on the Ni$_3$Al(111) surface and on the (0001) surface of sapphire. Adsorption of Tc has been studied for several surfaces, e.g., Cu(110),[21] Ag(111),[22] and Ag(110).[23] On these surfaces, monolayers with flat or nearly flat-lying Tc molecules were found without exception. Concerning insulator substrates, to our knowledge, only thicker Tc films were studied in the context of organic field effect transistors[24] and investigations on monolayers are still missing. Due to the smaller chemical reactivity of these surfaces, it is most feasible that for not too small coverages the Tc molecules adsorb in a *pin-cushion* arrangement with upright molecules, where the (001) bulk plane[25] is parallel to the surface, similar to pentacene.[26] Concerning its optical properties, Tc is a well-studied model molecule. Its fluorescence was investigated for thin vapor deposited films[27,28] and in large detail for single crystals (see Refs. 29 and 30 and references therein). The electronic S_0-S_1 transition is dipole allowed and polarized along the short molecular axis. At about 200 K, Tc crystals undergo a structural phase transition to a second also triclinic phase.[31,32] Likely due to this phase transition, a small redshift of the (0-0) line position from $F=18.800-18.900$ cm^{-1} at high temperatures to $F'=18.200-18.600$ cm^{-1} at low temperatures (60–100 K) occurs.[29,30] The phase transition is, however, not well reproducible and a wide range of transition temperatures has been reported in the literature (see Ref. 32), which is likely due to finite size and hysteresis effects. We note that from recent time-resolved measurements we have hints that the $F \rightarrow F'$ line shift involves a dynamical relaxation of the exciton that is only present for the Tc phase at low temperatures.[33]

We have chosen an ultrathin, epitaxial film of alumina (AlO$_x$) grown on the Ni$_3$Al(111) surface as a substrate surface for our experiments, because this substrate allows us to use electron based surface sensitive techniques. In addition, we also performed some control experiments on the sapphire (0001) surface. The AlO$_x$ film was prepared by annealing the Ni$_3$Al(111) surface in an oxygen atmosphere.[34] The oxidation process is self-terminating and leads to well-defined thin AlO$_x$ films, which consist of only two oxygen containing and two aluminum containing layers (oxygen terminated). The overall stoichiometry of Al:O is about 4:5.[35] The films are highly ordered and commensurate to the Ni$_3$Al(111) substrate, forming a large and complex superstructure with a hexagonal unit cell of 4.16×4.16 nm^2.[34,35] STM experiments show that the surface is very smooth with small step densities.[34] The band gap of the alumina film is estimated between 6.7 eV (Ref. 36) and 9 eV (Ref. 37) from scanning tunneling spectroscopy data. Since the alumina film is rather thin, electrons can tunnel through it to some extent, and hence the AlO$_x$ surface differs from that of an ideal insulator. As noted above, this property is utilized for photoelectron spectroscopy experiments, low energy electron diffraction (LEED), or STM experiments on the film. In combination

with the structural film properties, this makes AlO$_x$ films on Ni$_3$Al(111) ideally suited for surface experiments. In our experiments, however, it turned out that this charge tunneling appears to be also responsible for the luminescence quenching for Tc on the alumina surface.

The present paper extends the brief description of the photoluminescence results described earlier in Ref. 3. We report an additional structural analysis of the Tc films using high resolution low energy electron diffraction (see Sec. III A). In addition to the photoluminescence (PL) spectra obtained on the AlO$_x$ surface, we also include PL spectra obtained on the (0001) surface of a sapphire substrate. From the comparison of the spectra and their dependence on the Tc film thickness, we derive conclusions concerning the luminescence quenching on these surfaces.

II. EXPERIMENT

All experiments were performed under UHV. The samples were mounted on a sample holder at the end of a liquid He cryostat. The alumina film (AlO$_x$) was prepared by annealing a Ni$_3$Al(111) sample under an O$_2$ atmosphere according to the description given in Ref. 34. The structural quality of the alumina film was monitored by high resolution low energy electron diffraction [spot profile analysis low energy electron diffraction (SPALEED)], as reported in detail in Ref. 34. The (0001) oriented sapphire substrate was mechanically polished, cleaned by Ar$^+$ ion sputtering (at 650 K), and annealed by electron bombardment in an atmosphere of 1 $\times 10^{-8}$ mbar oxygen at 1150 K for about 10 min. This preparation routine is similar to those described in the literature,[38–41] although we could not go as high in temperature (1250–1650 K) due to experimental limitations. The SPALEED pattern showed the expected hexagonal structure (at 70 eV), but due to charging, the spots were strongly washed out.

The tetracene (Tc, see inset in Fig. 1) was obtained commercially and was purified by two cycles of gradient sublimation. Tc molecules were deposited onto the cold substrates at 45 to 100 K under UHV from a home-built Knudsen cell. At these low temperatures the molecules are expected to be immobile on the surface, and we can expect that *no* growth of ordered islands or crystallites occurs. As we will report, the experiments actually demonstrate that this expectation is correct. The film thickness was monitored by temperature programmed desorption (TPD) experiments (for experimental details, see Ref. 22). In the following we denote the film thickness in numbers of monolayers (ML) of *flat-lying* Tc molecules. Hereby one ML is equivalent to the surface density of Tc molecules which is obtained for the ordered α phase of Tc on the Ag(111) surface.[22] The surface area per one flat-lying Tc molecule in the α phase is 100.0 Å^2 and corresponds approximately to the footprint of one flat-lying molecule. We use this calibration for convenience, since for Tc films on Ag(111) the monolayer TPD signal of this phase could be separated from the multilayer TPD spectrum and allowed us to calibrate the measured desorption flux.[22] We note that 1 ML of flat-lying Tc molecules corresponds to a nominal film thickness of 2.36 Å, as calculated from the den-
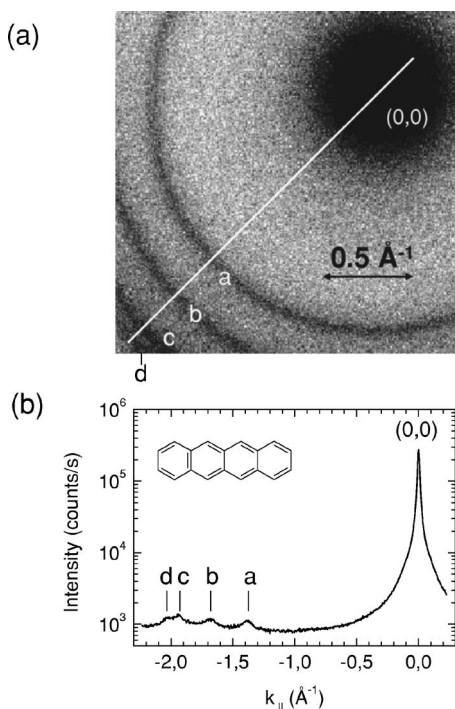
FIG. 1. (a) SPALEED pattern of a Tc film with a nominal thickness of 9 ML of flat-lying molecules deposited on a thin alumina film on Ni$_3$Al(111) at 45 K and annealed at 240 K. The electron energy was 25 eV. (b) Corresponding line scan along the line in (a). The indexing of the rings is given in Table I. The exact $k_\parallel$ values of the rings (see Table I) were obtained by a calibration with the SPA-LEED pattern of the alumina substrate. The inset shows the structure of the Tc molecule. Further details see text.

sity of a Tc bulk crystal.[25] SPALEED was also used for the investigation of the Tc films. For this purpose we used electron energies between 25 and 60 eV and beam currents of typically 2–10 nA. Conversion to k space was done by $k_0 = 2\pi/\lambda$.

The photoluminescence (PL) experiments were carried out directly after deposition of the molecules. For this purpose the sample was transferred by the manipulator into a small glass appendix of the UHV chamber, which is located within the path of the optical setup. Optical excitation was performed with an Ar laser at various wavelengths [458 nm (alumina substrate) and 476 nm (sapphire) and typical powers of 100 to 300 mW]. The spot diameter of the laser on the sample was typically 4 mm. The incidence angle of the excitation light was about 37° from the surface normal. The luminescent light was collected by a lens system with an acceptance angle of about 0.195 sr and focused into a monochromator (focal length 0.6 m, $f\#=7$). The light was finally recorded by a cooled photomultiplier (−40 °C), which was operated in the single photon counting mode. The dark count rate was approximately 50–200 counts/s. In order to suppress unwanted stray light from the exciting laser, a yellow glass filter (transmission for $\lambda \geqslant 515$ nm) was placed in front of the monochromator for the measurements made on sapphire.

III. RESULTS

A. Structural investigations of Tc films on AlO$_x$

After deposition of the tetracene (Tc) at 45 K, the SPALEED pattern showed no hints for ordered structures of the Tc. For very thin films (0.4 ML), the spots of the alumina film were strongly attenuated but still visible. For thicker films ($\geqslant 7$ ML), even the specular spot, i.e., the (0,0) spot, was fully washed out. This indicates that at these low substrate temperatures the molecules are immobile, and hence rough, disordered and closed Tc films are formed. From our data, the orientation of the molecules (i.e., that of the principle axes with respect to the substrate surface) cannot be derived. However, the shape of the molecule strongly suggests an adsorption planar to the surface, if isolated molecules are considered, since this yields a large contact face. Due to kinetic limitations, this orientation will be likely also maintained during film growth, as schematically indicated in Fig. 9 (see below). We will term such films as "as grown" in the following.

In a second preparation step, the films were heated up to 240 K (10–20 K/min) and annealed at this temperature for 1 min. (As described below, 240 K is well below the desorption temperature of Tc.) After cooling down to ~45 K, films with a nominal thickness $\geqslant 7$ ML showed a SPALEED pattern with distinct concentric rings around the (0,0) spot and *no* spots of the alumina substrate, as shown in Fig. 1(a). Hence the disordered Tc film had transformed into a closed film of Tc consisting of azimuthally randomly oriented, but ordered nanocrystalline Tc domains.

However, in some experiments, the SPALEED pattern of the clean alumina substrate was observed after the annealing step. Since no desorption occurred during the annealing, this indicates that small Tc crystallites with a small "footprint" had formed on the surface, which are "invisible" in the SPALEED pattern. Hence a dewetting of the substrate must have occurred. Finally we note that we did not achieve ordered films, if the films were too thick, i.e., about 20 ML. In this case the (0,0) spot was visible after the annealing cycle, but no rings or spots from the substrate were detected, which indicates that the films had become smoother, but were still disordered. We also did not obtain ordered Tc films, if the quality of the AlO$_x$ substrate surface was less perfect. These results indicate that the preparation of ordered, closed Tc films on AlO$_x$ is only possible within a small window of preparation parameters, and that the obtained films are only stable due to kinetic limitations.

From the SPALEED line scan in Fig. 1(b), it can be seen that the half width [full width at half maximum (FWHM) $=\Delta k_\parallel$] of the diffraction rings is about constant. This is a clear indication that the film consists of crystalline ordered domains, since for a fluidlike film (which would also yield concentric rings) the rings would smear out for higher values of $k_\parallel$. From the FWHM $\Delta k_\parallel$ of the rings in the radial direction, we can estimate the diameter $L=2\pi/\Delta k_\parallel$ of the ordered Tc domains to $L \sim 80$ Å. This value is about a factor of 4 smaller than the effective transfer width obtained from the FWHM of LEED spots of the clean alumina surface (~ 340 Å),[34] indicating that the size of the Tc domains is

TABLE I. Comparison of the ring diameters measured from Fig. 1 [rings (a) to (d)] and further SPALEED patterns [rings (e) and (f)] to ring diameters, which were calculated for the (001) plane of tetracene, assuming lattice constants $a = 7.6 \pm 0.2$ Å and $b = 6.1 \pm 0.2$ Å and an angle $\gamma = 90°$. Symmetry equivalent reflections are listed only once. The error of the measured g_{hk} values is ± 0.03 Å^{-1}.

Ring	g_{hk}^{measured} (Å^{-1})	$g_{hk}^{\text{calculated}}$ (Å^{-1})	(h, k)
(a)	1.32	1.32	(1,1)
(b)	1.69	1.65	(0,2)
(c)	1.94	1.95	(1,2)
(d)	2.03	2.06	(2,0)
(e)	2.58	2.64/2.68	(2,2)/(1,3)
(f)	3.16	3.09/3.20	(3,0)/(3,1)

likely limited by the growth kinetics, but not by the quality of the substrate.

The radii of the rings in $k_\parallel$ space, i.e., the g_{hk} values, were determined by a comparison with the very close mesh of the superstructure spots of the alumina film.[34] This procedure eliminates the nonlinearity of the SPALEED pattern at higher $k_\parallel$ values. For the indexing we used the procedure of Hull and Davy, which is usually used for indexing of Debye Scherrer rings.[42] We obtained a good fit of the g_{hk} values for a rectangular unit cell $(a, b, \gamma = 90°)$ for $a = 7.6 \pm 0.2$ Å and $b = 6.1 \pm 0.2$ Å (see Table I). These lattice parameters are close to those of the ab plane of bulk Tc measured at room temperature (RT) [$a = 7.91$ Å, $b = 6.06$ Å, $\gamma = 85.1°$ (Ref. 31)] and fit even better to the values of the similar low temperature (LT) phase of Tc [$a = 7.74$ Å, $b = 5.99$ Å, $\gamma = 86°$ (Refs. 31 and 32)]. If we set $\gamma = 86°$ in our analysis, we obtain the best fit of the measured g_{hk} for $a = 7.4$ Å and $b = 6.1$ Å. Hence we conclude that the structure of the domains parallel to the alumina surface is very similar to that of the ab plane in Tc bulk crystallites. However, the long vector a of the unit cell appears to be slightly reduced by about 5%, which may be related to a slightly different inclination angle of the molecules versus the substrate. A structure model (based on the RT-Tc phase for simplicity) is shown in Fig. 2. The molecules stand nearly vertical (upright) on the substrate with a tilt angle of ~15°, forming a herringbone structure with two

molecules per unit cell. The two-dimensional (2D) space group of the ab plane is nearly $p2gg$, since γ is close to 90°, which could explain why we did not observe the rings corresponding to the Miller indices (1,0) and (0,1). The diffraction ring of the indices (1,2) were possibly not observed due to intensity reasons. The vertical orientation of the molecules in this ordered phase causes that the footprint of the molecules is reduced with respect to that of flat-lying molecules by a factor of 4.3, and correspondingly a nominal thickness of 1 ML of flat lying corresponds to only 0.23 ML of standing molecules. We will term these annealed films as "ordered films" in the following.

Figure 3 displays a series of TPD spectra for different starting coverages for Tc films grown on the alumina film and on the sapphire (0001) surface. As far as we can judge, the spectra are identical in shape, indicating a very similar bonding of the Tc to both surface. The shift of the spectra on the sapphire surface with respect to those on the AlO$_x$ film by about 50 K is likely due to an offset in the temperature measurement due to a weak thermal contact of the thermocouple to the sapphire sample, and hence not meaningful. The TPD spectra show a common rising edge and a sharp cutoff on the high temperature side. This reveals a zero order desorption kinetics, as expected for multilayer films. The Tc can be fully desorbed from both substrates. As a consequence, the LEED substrate spots are visible again after the annealing cycle. There are no indications for a separated desorption peak of the monolayer, as it is for instance seen for Tc adsorbed on the Ag(111) surface.[22] We interpret this as an indication for a very weak bonding of the Tc to these surfaces. From a leading edge analysis of the TPD spectra measured on the alumina film and the sapphire surface, we find that the desorption energy E_d saturates at about 20 ML and converges then to 130–135 kJ mol^{-1} at about 90 ML. This value is well compatible with the value of $E_d = 120$–130 kJ mol^{-1} found for Tc films on the Ag(111) surface.[22]

B. Photoluminescence

1. Photoluminescence spectra of Tc on the AlO$_x$ surface

Figure 4 displays a typical PL spectrum which was obtained for a 7 ML thick Tc film *after* the annealing step and subsequent cooling to 45 K [curve (a) in Fig. 4]. The maxi-
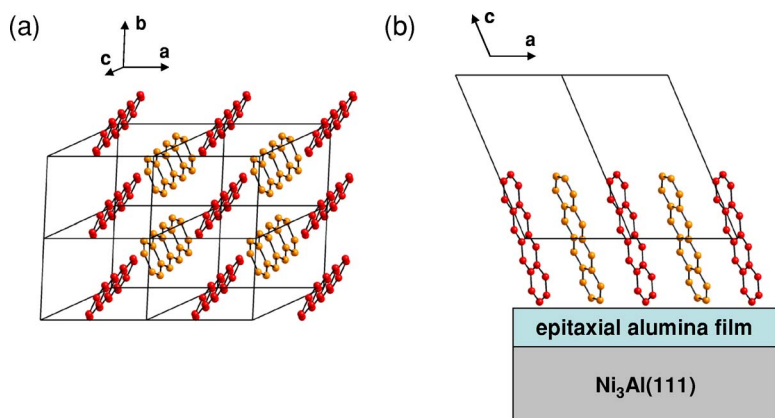

FIG. 2. (Color online) Structure model of the ordered Tc film on the alumina film on Ni$_3$Al(111): (a) top view, (b) side view.
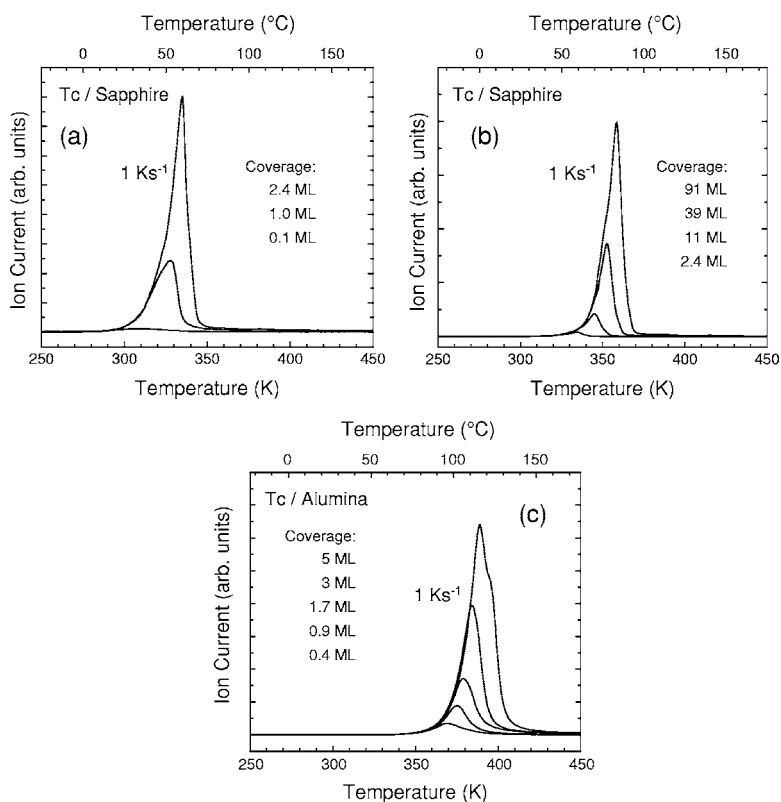
FIG. 3. Temperature programmed desorption spectra of Tc films with different nominal thickness on the sapphire (0001) surface (a) and (b); and on a thin alumina film on $Ni_3Al(111)$ (c). The vertical axis of (b) is compressed with respect to that of (a) by a factor of 55. The ion currents were recorded at m/z=228 amu.

mum is at 18 600 cm^{-1}. This position agrees with the one observed for Tc crystals at low temperatures[30] and is explained by the 0-0 transition of the free exciton (F') in the low temperature (LT) Tc phase. This result thus corroborates the above conclusion from LEED that the Tc molecules have ordered in the LT Tc bulk phase. The intensity on the low energy side of the main peak, which exhibits several shoulders, is *not* due to intrinsic decay channels, i.e., vibronic replicas of the 0-0 transition. The shoulder at ~18 000 cm^{-1} (peak 1) is tentatively assigned to the decay of a self-trapped exciton (ST), as it had been proposed for single crystals.[29] The smaller shoulders at ~17 000 cm^{-1} (peak 2) and ~15 500 cm^{-1} (peak 3) are due to luminescence from radiative traps at structural defects. This interpretation is supported from the observed temperature variation of the spectrum (see below) and our observation that these spectral features varied in their relative intensity with respect to the main peak, if the preparation conditions were changed. For the variation of the film thickness, this is for instance demonstrated by curve (b) in Fig. 4, which shows a strong contribution of the ST exciton. The role of the surface quality becomes also evident from the experiments on sapphire, which are reported in the next section.

The change upon variation of the temperature of the 7 ML spectrum is shown in Fig. 5. At about 80 K the position of the maximum starts to shift by 200 cm^{-1} to higher energies ($F \rightarrow F'$). This is consistent with the observation for single Tc crystals, where the same spectral shift of the free exciton was observed and interpreted as a consequence of the phase transition from the LT to the RT phase. The fact that the transition occurs at rather low temperatures here (80 K versus ~200 K for single crystals) is likely a consequence of

finite size effects and/or the influence of the underlying substrate. As can be seen in Fig. 5, the intensity on the low energy side of the main peak is strongly diminished at higher temperatures, which supports the above conclusion that it results from nonintrinsic decay channels, which are less effective at higher temperatures. In the spectrum at 200 K, only two faint shoulders at 16 200 and 17 000 cm^{-1} are left, which we assign to the vibronic replicas (0-2) and (0-1) of the F exciton.

Remarkably, we did not observe a PL signal for thin Tc films on the alumina surface prior to the annealing step. As an example for a spectrum of such an as-grown film, the spectrum of the 7 ML film that we discussed above, is shown in Fig. 4 [curve (c)]. The spectrum is *identical* to the spectrum of the clean alumina surface [curve (d)], which can be considered as the background spectrum. This spectrum is mainly due to stray light from the exciting laser, the count rate being 10 to 15 times the dark rate of the photomultiplier. The small peaks above 18 200 cm^{-1} are artifacts due to the experimental setup. Possibly they are due to small amounts of Tc that were adsorbed on the inside of the glass head. From the reported spectra, we hence derive that Tc films grown at low temperatures are *nonluminescent*, and hence the luminescence must be strongly quenched (at least as much that it falls below the detection limit of our experiment). Remarkably, this quenching is not only observed for monolayer films but has been found for thicker films up to 7 ML. The corresponding spectra prior and after annealing for a thinner film with 1.2 ML were shown in Ref. 3 (see also comment in Ref. 43). Two different reasons can be envisaged for this quenching: (i) structural disorder within the films, and (ii) an electronic interaction of the excited molecules with the substrate.
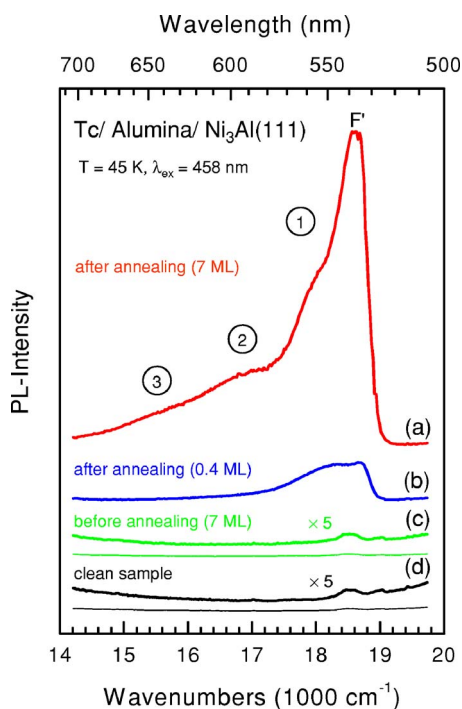
FIG. 4. (Color online) Photoluminescence spectra of *thin* Tc films on the alumina surface. (a) and (b) spectra of Tc films with a nominal thicknesses of 7 ML and 0.4 ML after an additional slow warming cycle up to 240 K with about 10 K min^{-1} (c) after deposition of nominally 7 ML of flat-lying Tc molecules at 45 K. (d) spectrum of the clean alumina surface for comparison. All spectra were measured at 45 K. The excitation wavelength was 458 nm (21 800 cm^{-1}, 2.702 eV). The small peak at about 18 500 cm^{-1} in the magnified spectra (d) and (c) is an artifact, likely from the glass window of the UHV chamber. The very small peak at 19 500 cm^{-1} is a plasma line from the Ar laser. The spectra are vertically shifted against each other for clarity. For the discussion of the marked peaks 1–3 and F see text.

2. Photoluminescence spectra of Tc on the sapphire (0001) surface

The PL spectra recorded for Tc films deposited on the sapphire (0001) surface are displayed in Figs. 6 and 7. On sapphire (0001), we also observe a significant luminescence of the clean substrate ("autoluminescence") below 16 500 cm^{-1} (see Figs. 6 and 7). It is likely due to impurities in the sapphire or structural defects remnant from the sputtering process. We start with the discussion of a thicker Tc film for simplicity. In Fig. 7 the PL spectra of a relatively thick film (20 ML, ∼50 Å) are shown for the as-grown film and the same film after the annealing step to 240 K. Both spectra consist of the three broad peaks at the same positions, but with varying contributions. Upon annealing, peak 1 gains relative intensity with respect to the others.

The peak positions (1–3) agree within error with those that had been observed for the shoulders in the above discussed 7 ML spectrum on AlO$_x$ in Fig. 4. Hence we make the same assignment here: decay via a self-trapped exciton (1) and two radiative traps (2 and 3). A peak corresponding to the free exciton (F or F') is missing for these films. There-
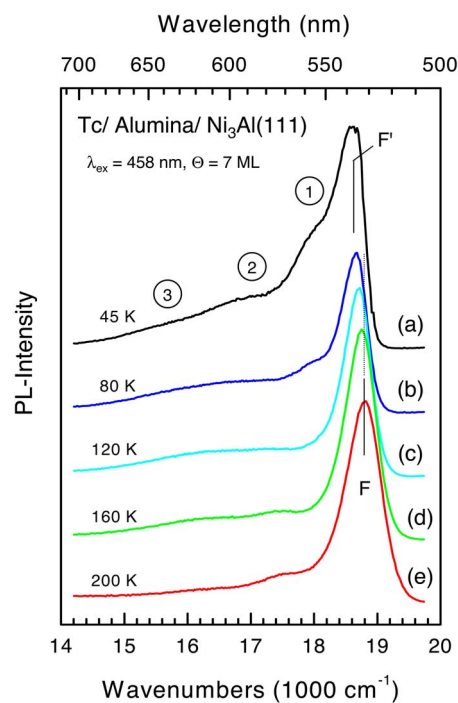
FIG. 5. (Color online) Photoluminescence spectra of the 7 ML Tc film on the alumina surface for various temperatures after preparation at a growth temperature of 45 K and an additional annealing cycle to 240 K. The excitation wavelength was 458 nm (21 800 cm^{-1}, 2.702 eV). The spectra were measured from low to high temperatures. The changes in the spectra as a function of temperature were found to be reversible in temperature. The spectra are vertically shifted against each other for clarity. For further details, see text.

fore, we conclude that the thick film is strongly disordered prior and still after the annealing step. Annealing reduced this disorder only to some extent, which leads to annihilation of some of the nonradiative traps, as can be seen from the increase of the integrated intensity by about a factor of 3.

Figure 6 displays the PL spectra of very thin Tc films (1 and 2.3 ML) on sapphire. Curves (a) to (c) in Fig. 6 show the spectra of the annealed films, curves (d) and (e) spectra of two as-grown films, and curve (f) the background spectrum of the clean sapphire surface. Note that the spectra (d), (e), and (f) are displayed with a vertical scale that has been extended by a factor of 30 in addition to the original spectra (thin lines), which are on the same scale as all other spectra. First of all we find, that the spectra of the annealed films are very similar to that of the 7 ML film on AlO$_x$ (Fig. 4), which indicates a similar structural order. Most interesting are the PL spectra of the two as-grown films [curves (d) and (e) in Fig. 6]. The comparison with the background spectrum of the clean sample shows that for Tc, only a very small, broad, and structureless band is found between 16 500 and 19 000 cm^{-1}, which varies slightly in intensity for the different experimental runs, as illustrated by the curves (d) and (e) in Fig. 6. None of the spectral features which are significant for the luminescence of Tc are observed. Concerning the integrated intensity (from 16 500 to 19 000 cm^{-1}), the intensity gain upon annealing is about a factor of 30. Hence we have to
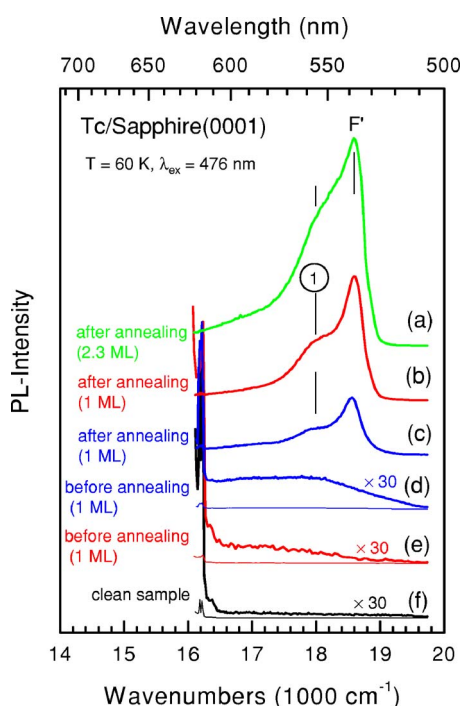
FIG. 6. (Color online) Photoluminescence spectra of several *thin* Tc films with nominal thicknesses in the range of 1 to 2.3 ML on the sapphire (0001) surface. (a)–(c): spectra after an additional annealing cycle at 240 K; (d) and (e): two spectra measured from the as-grown films (both 1 ML); (f) luminescence of the clean sapphire surface. The spectra (c) and (b) correspond to (d) and (e), respectively. The spectra (c)/(d) and (b)/(e) demonstrate the variation between different experimental runs. All spectra (a)–(f) were measured at 60 K. The excitation wavelength was 476 nm (21 010 cm^{-1}, 2.60 eV). The spectra are vertically shifted against each other for clarity.

conclude that (i) the luminescence of thin as-grown Tc films on sapphire is strongly quenched, and (ii) that the spectral features are "washed out" into a featureless "band."

Interestingly, the intensity of the autoluminescence of the sapphire is unaltered upon the deposition of the Tc at low temperature. However, it is reduced by a factor of about 3 when the Tc film is annealed. The origin for this effect is not clear yet.

3. Dependence of the integrated PL yield as a function of the film thickness

Figure 8 summarizes the photoluminescence intensities integrated over the wave numbers as a function of the nominal film thickness for both kinds of substrates on a double logarithmic scale. The integration was performed from 16 500 cm^{-1} to 19 700 cm^{-1} for the sapphire sample, and from 13 600 cm^{-1} to 19 700 cm^{-1} for the AlO$_x$ sample. The values were normalized to the excitation power of the laser and to the slit width of the spectrometer. The resulting error of the integrated intensities is estimated by ±30% (see Fig. 8), and is mainly due to variations in the efficiency of light collection into the spectrometer for the different experimental runs. On the lower x axis of Fig. 8, the nominal film thickness is denoted in numbers of ML of flat-lying mol-
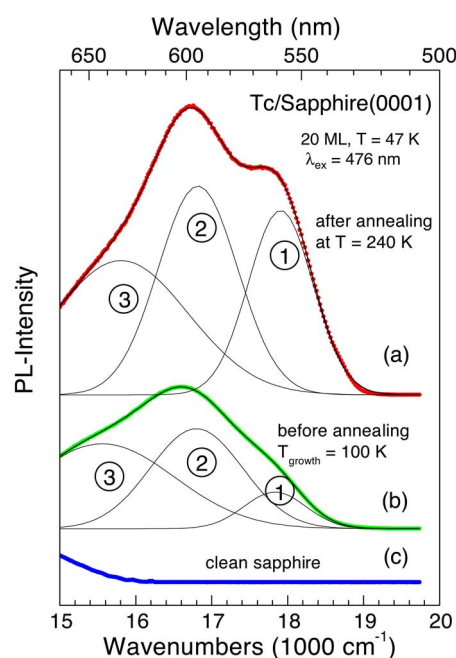
FIG. 7. (Color online) Photoluminescence spectra of a *thick* Tc film (nominal film thickness 20 ML) on the sapphire (0001) surface. (a) spectrum after an additional annealing cycle at 240 K; (b) Spectrum measured for the as-grown film; (c) luminescence of the clean sapphire surface. The spectra were measured at 47 K. The excitation wavelength was 476 nm (21 010 cm^{-1}, 2.60 eV). The spectra are vertically shifted against each other for clarity. With respect to Fig. 6, the y axis is compressed by a factor of 25.

ecules. Since the LEED results for the films on the AlO$_x$ surface indicate that the molecular orientation changes upon annealing, the nominal film thickness is additionally denoted in numbers of ML of upright standing molecules on the top x axis (see Sec. III A above).

We start with the interpretation of the results obtained for the *annealed* films. The most evident conclusion to be drawn from Fig. 8 is that the integrated luminescence of the annealed films on both the AlO$_x$ and the sapphire surface is about proportional to the nominal film thickness, and therefore to the amount of deposited Tc. This is indicated by the linear fit in Fig. 8. The proportionality holds even for very small coverages, i.e., 0.2 ML of presumably upright standing molecules on both surfaces. The result simply implies that the luminescence of the molecules is about constant, irrespective of their distance to the underlying surface. In particular, we have to conclude that Tc molecules in direct contact to the substrates are luminescent, i.e., in the first monolayer. This finding is in clear contrast to the situation found for Tc, quaterthiophene, or PTCDA films grown on the Ag(111) surface. On the Ag(111) surface, no luminescence at all is observed for films of the noted molecules up to a thickness of two complete monolayers of flat-lying molecules. Hence for annealed Tc films on the AlO$_x$ and sapphire surface, with presumably an upright orientation of the long molecular axis with respect to the surface, *no* fast luminescence quenching occurs. This finding is in agreement with what is expected for a wide gap insulator substrate. Of course,
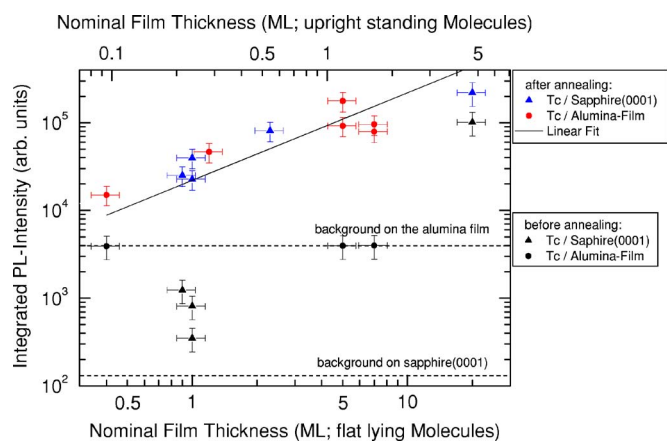
FIG. 8. (Color online) Integrated photoluminescence intensity as a function of the nominal film thickness of Tc films before (black symbols) and after annealing (red/blue symbols) on the alumina substrate (circles) and sapphire (triangles). The values were normalized to the power of the exciting laser beam. The background levels measured on the clean substrates are indicated by dashed lines. For the alumina substrate, the background is higher due to stray light from the exciting laser, which was suppressed for the sapphire sample by a filter (see text). The solid line is a linear fit (y =const.$\times$ film thickness) to the data. For further details, see text.
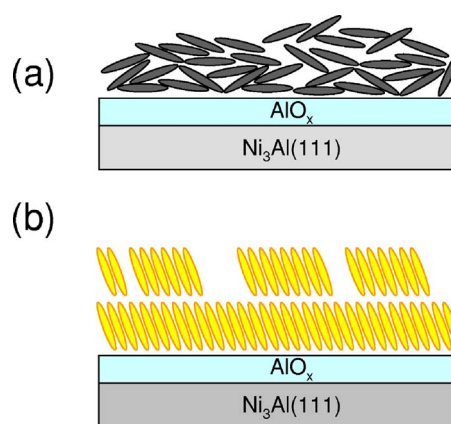

FIG. 9. (Color online) Schematic sketch of the geometric arrangement of the molecules on the substrate prior (a) and post (b) annealing. The gray molecules indicate molecules that do not luminesce, the yellow molecules are those molecules that luminesce after annealing.

quenching due to energy transfer to the image dipole in the metallic Ni_3Al substrate, as described by the theory of Chance *et al.*,[13] is expected here, too. The efficiency of this quenching mechanism depends on the distance of the molecules with respect to the Ni_3Al substrate, and has been observed, e.g., for rhodamine on Ag substrates covered by thin sputtered AlO_x layers.[18] However, in our experiment, due to the constant space separation by the AlO_x film, the variation of this quenching rate within the considered thickness range of the Tc layers is likely within the error bar of the data and hence not observed.

Concerning the *as-grown* films the situation is, however, significantly different. We first interpret the results for films grown on the alumina surface. As can be seen for the example in Fig. 4, we find that up to a thickness of 7 ML of flat-lying molecules, the luminescence spectra are identical with those measured for the clean sample. Hence the integrated luminescence data points fall onto the level of the background luminescence, which is obtained from integration of the luminescence spectrum of the clean sample (see Fig. 8). (We note that this background signal is nonzero, likely due to stray light from the exciting laser beam which is reflected at the sample surface.) As a consequence, a fast quenching mechanism must exist for the disordered films on AlO_x. This mechanism is not only effective on the first molecules in direct vicinity with the substrate but also for higher layers, since we have observed the quenching for a film with a nominal thickness of 7 ML of flat-lying molecules. Figure 9 represents a schematic illustration of the Tc film on the alumina surface prior and after annealing.

On the sapphire (0001) surface, the measurements for the as-grown films were in particular taken for the monolayer range, i.e., a nominal coverage of 1 ML (see Fig. 8). As described above, a very weak and broad luminescence

"band" is observed. With respect to the annealed film the integrated intensity of this band is less than 5%, but is clearly above the background. Since the high energy edge of this band ($\sim$18 000–19 000 cm^{-1}) is about at the position of the electronic origin (0-0) of the Tc luminescence in the ordered films, we assign this band to luminescence of Tc molecules, which is very strongly inhomogenously broadened due to structural disorder at the interface. In different nominally identical preparation routines, differences in the shape and integrated intensity (factor of 5) of the band were observed (see above). This possibly indicates that small differences in the flux, the sample temperature, or the preparation of the clean sapphire surface plays a role for the luminescence of the Tc molecules in the monolayer.

IV. DISCUSSION

For the sapphire surface, luminescence is observed both for the as-grown and the annealed films. Hence an ultrafast luminescence quenching mechanism via charge transfer from the S_1-excited Tc molecule must be absent or strongly reduced here. This finding is in agreement with what is expected from the large band gap of about 8 eV of sapphire (α-Al_2O_3).[44] This large band gap does not permit transfer of an electron from the lowest unoccupied molecular orbital (LUMO) of the S_1-excited Tc molecule into the conduction band of the substrate, or transfer of an electron from the valence band into the highest occupied molecular orbital (HOMO) (see Fig. 3 in Ref. 3). Hence a fast luminescence quenching mechanism is absent here and the luminescence can be observed. Photoluminescence on wide gap materials was observed, e.g., for rhodamine on quartz[16] or PTCDA on mica.[15] However, we note that the luminescence of the as-grown Tc films is very broad, likely due to disorder.

The very low luminescence yield of the as grown Tc films is a bit disappointing so far, since it limits luminescence experiments on *isolated* Tc molecules, which are commonly prepared by depositing the molecules at these low tempera-

tures, where the molecular diffusion is small and aggregation is thus hindered. Annealing of the films does increase the luminescence significantly. However, as we can deduce from the structural data obtained on the AlO_x surface and the identical shapes of the PL spectra of the annealed films on AlO_x and sapphire, annealing leads to a change in the molecular orientation and to the formation of Tc aggregates (islands or crystallites) on both surfaces. Hence after annealing, the strong luminescence intensity stems from aggregates of Tc molecules, but not from isolated molecules on this surface.

The most interesting situation occurs on the AlO_x surface. Two mayor findings have to be explained here: (i) which mechanisms lead to the unexpected quenching of the as grown monolayer and multilayer films, and (ii) how does the annealing change this? To answer these questions, we briefly summarize some of the electronic properties of AlO_x films on $Ni_3Al(111)$. These were investigated by scanning tunneling spectroscopy (STS) by Maroutian *et al.*[37] and recently in further detail by Degen.[36] For large tip sample distances (i.e., if the feedback loop is opened at $U_{sample}=3-4$ V, 100 pA) a zero density of states is found between −4 and 2.5 eV (with respect to the Fermi energy), and tails of the valence and conduction band edges rising at the end of this range. Hence the AlO_x film apparently exhibits a band gap of about 6.5 eV, similar in width to the band gap of sapphire. On the basis of this data, we would hence expect to find the same situation as on the sapphire (0001) surface and *no* mechanism explaining the total absence of the luminescence for the as-grown films would be discernible.

However, recently, Degen[36] observed that at small bias voltages (e.g., $U_{sample}=190$ meV), i.e., close to the Fermi level, it is possible to image the Al atoms at the $AlO_x/Ni_3Al(111)$ interface through the AlO_x film. Hence the metallic wave functions of the underlying $Ni_3Al(111)$ substrate "leak" through the AlO_x film into the vacuum. This is also seen from the STS spectra taken for small tip sample distances (e.g., if the feedback loop is opened at $U_{sample}=190$ meV, 70 pA), which show the density of states corresponding to the uncovered $Ni_3Al(111)$ surface at energies between −1 and 1 eV.[36,45]

Concerning the explanation of the observed luminescence quenching for the as-grown Tc films, the leaking of wave functions close through the AlO_x allows a quenching mechanism by charge transfer. A schematic energy diagram of the $Tc/AlO_x/Ni_3Al(111)$ interface is shown in Fig. 10. The positions of the valence and conduction band edges of the AlO_x film are taken from ultraviolet photoemission spectroscopy data[46] and scanning tunneling spectroscopy data,[37] respectively. The position of the HOMO of the Tc was estimated with the help of the ionization energy of Tc in the gas phase (6.9 eV).[47] On a thin insulator film, this value is hardly changed by screening effects due to the underlying metal substrate,[48] but this is not known in detail for this system at present. Also unknown is the shift of the vacuum level at the AlO_x/Tc interface due to an interface dipole. In Fig. 10 the unknown offset in the vacuum level is indicated by the "?." Typical experimentally determined vacuum level shifts are up to 1 eV for physisorbed systems.[49] However, on the basis of the known energy levels and their noted uncertainty, elec-
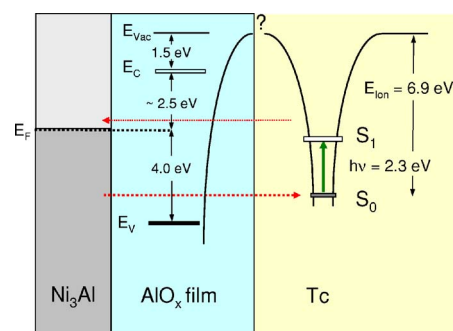

FIG. 10. (Color online) Schematic energy diagram for Tc adsorbed on an epitaxial thin AlO_x film on $Ni_3Al(111)$. The energy levels are taken from the references given in the text. The dotted (red) arrows indicate likely charge transfer process between the excited Tc molecule and the substrate states leaking through the AlO_x film, after an optical excitation, indicated by the vertical (green) arrow. The question mark indicates a possible shift of the vacuum level at the Tc/AlO_x interface due to the interface bonding. The exact size of this shift is unknown so far.

tron transfer from the S_1 excited molecule into empty $Ni_3Al(111)$ states, and/or in particular from the occupied $Ni_3Al(111)$ states into the half-emptied HOMO of the excited molecule appears to be a likely and energetically possibly decay channel for Tc on the AlO_x film. Such a charge transfer via electron tunneling across the AlO_x film will be in particular highly efficient for *flat-lying* Tc molecules, for which the overlap of the π orbitals (which are located on both sides of the planar molecule) with wave function tails of substrate states is high. We propose that this mechanism is relevant for about the first two layers of flat-lying Tc molecules close to the interface, similar as for other flat-lying π conjugated molecules on the Ag(111) surface.[2] This charge transfer (CT) mechanism hence explains the luminescence quenching for the as-grown films. Obviously, the time constant τ_{CT} for the charge transfer must be significantly faster than the fluorescence decay time τ of the Tc layers. If we estimate the later by the τ value measured for Tc films,[28,33] which is about 80 ps, and deduce from our data that the luminescence yield Φ' on the AlO_x for the nonannealed films is by at least a factor of 10^{-2} smaller compared to the annealed films, it follows that $\tau_{CT} \leq 10^{-2} \tau = 0.8$ ps.[50] We note that we formerly explained the luminescence quenching by excitation of a vibronic mode of the molecule with respect to the interface leading to fast de-excitation.[3] However, in the light of the small luminescence present on the sapphire surface, an explanation based on this mechanism alone appears unlikely.

In order to be able to explain the quenching of *thicker* as-grown film on AlO_x, there must be one or several additional mechanisms, since the substrate wave function is damped at distances further away from the surface, as found by STS (see above),[34] and the charge transfer rate should thus be strongly suppressed. The most likely mechanism is a resonant (Förster type) energy transfer from molecules further away from the substrate to molecules closer to the substrate, for which the decay occurs nonluminescent. Since the bonding of molecules at the Tc/AlO_x interface is only weak,

the energetic states, in particular the exited S_1 state, should be only modified to a little extent and an effective transfer of the exciton via resonance coupling should be thus possible. However, a diffusive (due to the disorder) exciton migration from molecules further away from the interface to molecules close to the interface could also occur. Both mentioned processes in combination with nonradiative on-site decay processes, due to structural disorder, cause that the luminescence yield becomes so low that it falls below the detection level of our experiment.

Finally, we have to interpret the significant rise of the luminescence yield on AlO_x upon annealing of the films. As described above, annealing causes structural ordering of the as-grown Tc films with a concomitant change of the molecular orientation from a preferential planar orientation to an upright orientation (see Fig. 9). This change of the molecular orientation was recently also derived from high resolution electron loss spectroscopy data by Soubatch *et al.*[51] For the rise in the luminescence yield, two explanations have to be discussed. The first is based on the scenario that the annealing leads to dewetting of the interface and to formation of Tc crystallites with a high aspect ratio (small footprint) which effectively increases the average distance of molecules to the Tc/AlO_x interface and thus suppresses the interface quenching. In combination with a reduction of the nonradiative decay rate due to disorder, this could indeed explain the rise in the PL yield upon annealing. However, we feel that this explanation is not sufficient, because we observed luminescence for very thin annealed films of only 0.1 ML thickness of upright oriented molecules, and we found from SPALEED (see Sec. III A) that, for instance, a 1.6 ML thick annealed film of upright standing molecules (=7 ML of flat-lying molecules) forms a luminescent and closed film. Hence a dewetting as the only explanation is unlikely.

A second alternative explanation is that the change in the molecular orientation from a preferential planar orientation to an upright orientation upon annealing leads to a significant decrease of the probability for charge transfer of the excited molecules to the $Ni_3Al(111)$ substrate. The presumed reason is that the upright oriented Tc molecules exhibit a much smaller overlap of the involved π orbitals with metal wave functions leaking through the AlO_x film compared to flat-lying molecules. At present, we have no further evidence for the correctness of this model. Nevertheless, we expect that other spectroscopies with time resolution in the subpicosecond range, e.g., two-photon photoemission spectroscopy (2PPE),[52] or resonant Auger electron spectroscopy,[53] see differences for planar and upright Tc molecules on AlO_x. In addition, spectral changes may be expected in photoelectron spectra [ultraviolet photoemission spectroscopy (UPS) or x-ray photoemission spectroscopy (XPS)] for both types of molecules due to different time constants of the final state screening.

V. SUMMARY

Tetracene deposited at low temperatures on highly ordered thin AlO_x films grown on $Ni_3Al(111)$ yields disordered and nonluminescent films. The luminescence quenching likely occurs by charge transfer across the AlO_x films to the underlying metal substrate. Annealing yields ordered films with a bulklike structure and upright oriented molecules, which show luminescence from all layers. The absence of the luminescence quenching for the annealed films is explained by the reduction of the charge transfer probability due to the change in the molecular orientation from lying to upright. Concomitant experiments on sapphire (0001) show luminescence for the as-grown *and* the annealed films. However, the luminescence of the as-grown films is very weak and extremely broadened; both effects are explained by structural disorder.

ACKNOWLEDGMENTS

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