Copper oxide phases probed via plasmonic light emission in the STM

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Keywords: STM luminescence, plasmon, exciton, cuprous oxide, photon mapping

Supplementary material for this article is available online

Abstract

Luminescence spectroscopy with a scanning tunnelling microscope (STM) is employed to differentiate bulk-type Cu2O from a Cu3O2 surface oxide at the nanometre scale. Although plasmonic modes in the tunnelling gap are responsible for the emission response in both cases, the luminescence cross-section shows a characteristic dependence on bias voltage for the two oxide phases. On the Cu3O2 surface oxide, the emission yield peaks at the 1st field emission resonance of the STM junction, when particularly high inelastic tunnelling rates are realized between tip and sample. On Cu2O(111) patches, on the other hand, direct and defect-mediated electron recombination from the oxide conduction to the valence band is responsible for plasmon excitations in the STM cavity. Given the different excitation mechanisms, Cu2O and Cu3O2 oxide regions become distinguishable in bias-dependent STM luminescence maps with nanometre precision. We expect this optical contrast scheme to be applicable whenever blends of dielectric materials with different band gaps coexist on the surface.

1. Introduction

Optical spectroscopy is a powerful tool to probe the electronic structure of solids. It provides insights into excited-state energy surfaces, many-particle states and interference effects. Spatially resolving techniques are required to study the interplay of structural and optical properties of matter [1]. Most optical modes exhibit a pronounced spatial dependence and vary at length scales much shorter than the wavelength of light. Examples are the optical response of inhomogeneous materials, phase mixtures and blends, plasmon confinement in nanoparticles and exciton trapping at structural defects [2].

Scanning tunnelling microscopy (STM) is a central tool to study optical activity at atomic length scales. The method has seen enormous progress in recent years and was employed to probe plasmons in single particles [3–5], photon emission of molecules [6, 7], dielectrics [8, 9], and 2D materials [10, 11], and Raman fingerprints of organic species [12, 13]. More recently, the electromagnetic coupling between localized excitons and the tip-induced plasmons has moved into the focus of research [14, 15]. In all these cases, the enormous field enhancement in the tip/sample cavity helped detecting even weak optical signals [16, 17]. Not surprisingly, noble metals, e.g. silver and gold were the typical materials used in these experiments [18, 19]. Conversely, dielectric systems are rarely investigated despite their relevance for photocatalytic and photovoltaic applications. Especially oxides exhibit a notoriously inhomogeneous optical response due to poorly screened defects, colour centres and impurities [20, 21], calling for an examination with local techniques. Nonetheless, only a few oxides have been studied by STM luminescence so far, e.g. ZnO [9, 22, 23], TiO2 [24], and MgO [25, 26].

Cuprous oxide (Cu2O) is a particularly fascinating optical material. It exhibits a direct, yet parity forbidden band gap in the visible range (2.15 eV) [27, 28] and a well-developed system of para- and ortho-excitons with more than ten resolvable replica [29, 30]. Moreover, several defect-related emission
Figure 1. (a) STM overview image of an oxide mixture on Au(111), comprising thick Cu$_2$O and thin Cu$_3$O$_2$ patches ($U_B = 2.0$ V, $I = 50$ pA, $100 \times 100$ nm$^2$). Close-up images of (b) a Cu$_2$O island with Cu$_4$O nano-pyramids in $(\sqrt{3} \times \sqrt{3})$ R$30^\circ$ arrangement and (c) the Cu$_3$O$_2$ surface oxide made of strained Cu–O six-rings ($11.5 \times 11.5$ nm$^2$). (d) LEED pattern of the mixed film with double spots due to the deviating lattice parameters of Cu$_2$O and Cu$_3$O$_2$. (e) STM conductance spectra of thick Cu$_2$O (blue) and thin Cu$_3$O$_2$ (orange curve), acquired at 2.5 V setpoint bias. Whereas the Cu$_2$O spectrum shows the characteristic signature of a p-type conductor with 2.0 V band gap, a symmetric gap configuration is revealed for the surface oxide.

lines can be detected, with the ones related to O and Cu vacancies being the most intense [31]. The Cu$_2$O luminescence is thus expected to show high spatial variability, however, no local optical data are available so far. This is particularly surprising, as the material is considered to be a reference p-type conductor for photovoltaic devices. Reported efficiencies of Cu$_2$O/ZnO solar cells are below 2% yet, most likely due to parasitic exciton decay at lattice defects [32].

We have recently developed a high-pressure oxidation scheme to fabricate well-ordered Cu$_2$O films on Au(111) supports [33]. The films can be prepared with arbitrarily thicknesses and are sufficiently flat and conductive to enable STM measurements. Their surface is homogenously covered with a $(\sqrt{3} \times \sqrt{3})$ R$30^\circ$ reconstruction, similar to one found on bulk crystals. High resolution STM images combined with density functional theory calculations allowed us to derive a structure model of the reconstruction, in which Cu$_4$O nano-pyramids bind to every third Cu–O six ring of the bulk-cut surface [34]. This reduces the number of dangling bond states to a minimum and makes the reconstruction particularly stable. In this work, STM luminescence spectroscopy and mapping is employed to explore the optical properties of Cu$_2$O(111) films with nanometre spatial resolution. By analysing elastic and inelastic tunnelling channels, we address the question whether the emission response is mediated by Cu$_2$O excitons or coupled plasmons in the STM junction. Moreover, a purely optical pathway is demonstrated to discriminate different oxide phases on the surface. Our experiments demonstrate the unique capabilities of STM luminescence to unravel the optical properties even of dielectric surfaces.

2. Experimental

The experiments have been carried out in an ultrahigh-vacuum setup ($p \sim 2 \times 10^{-10}$ mbar), equipped with a Beetle-type microscope operated at liquid-nitrogen temperature and standard surface-science tools for sample preparation and analysis. Photon emission from the STM junction was collected with a lens system and detected with a Peltier-cooled photomultiplier tube and a charge-coupled device for integral and spectral analysis, respectively. Differential conductance ($dI/dV$) spectra were acquired with a lock-in amplifier at $\sim 14$ mV modulation bias and $\sim 1.8$ kHz. Electrochemically etched gold wires were used as tips.

The Cu$_2$O films were fabricated by dosing 10 Cu layers from an e-beam evaporator onto a sputtered and annealed Au(111) single crystal, followed by an oxidation in 50 mbar O$_2$ (purity 99.9999%) at 450 K in a designated high-pressure cell [33]. The films were crystallized by post-annealing at 700 K in front of an O$_2$ nozzle at $10^{-4}$ mbar local pressure. At this temperature, the oxide phase-separates into bulk-like Cu$_2$O patches and a Cu$_3$O$_2$ wetting oxide, according to the Stranski–Krastanov scheme (figure 1(a)) [35]. The dewetting transition was enforced here to produce an electronically and optically inhomogeneous oxide system, while single-phase Cu$_2$O can be prepared by heating at 600 K.
The Cu₂O phase, being identified by x-ray photoelectron spectroscopy [33], is made of large crystallites of 20–50 nm diameter and 1–3 nm height (figure 1(a)). They are (111)-oriented and covered with a \((\sqrt{3} \times \sqrt{3})\) R30° reconstruction, being imaged as incomplete array of shamrock-type protrusions with 10.5 Å periodicity in the STM (figure 1(b)). These maxima locate in the centre of every third Cu–O six-ring of bulk-cut Cu₂O(111). They are made up of Cu₂O nano-pyramids with three Cu atoms pointing towards the unsaturated O\(_{cu}\) ions of the hosting ring and a fourth one sitting below. [34] A capping O ion saturates the Cu dangling bonds and stabilizes the pyramidal configuration. The Cu–O six-rings next to the nano-pyramids remain empty, as the binding potential of their O\(_{cu}\) ions is already consumed. The \((\sqrt{3} \times \sqrt{3})\) R30° reconstruction is energetically preferred in a wide range of oxygen chemical potentials and found on (111)-cut bulk crystals as well. [36]

The Cu₂O wetting oxide, on the other hand, comprises a honeycomb lattice of Cu–O six rings and grows in (2 × 2) registry with the Au(111) support (figure 1(c)) [35]. Its lattice parameter is \(\sim 4.5\%\) smaller than the one of Cu₂O (6.1 Å), as reflected by the split reflexes in low-energy electron diffraction (LEED) (figure 1(d)). While the Cu ions occupy hollow sites in the Au(111) surface, the O ions alternatingly locate in top and bridge positions and induce a substantial film buckling. Thickening of the Cu₃O₂ layer towards bulk Cu₂O is inhibited by the substantial lattice mismatch to the Au(111) support. The most abundant point defects in the Cu₃O₂ wetting oxide are Cu ad-atoms filling a few Cu–O six rings (figure 1(e)).

The two oxide phases also differ in their electronic structure, as reflected in the \(dI/dV\) spectra shown in figure 1(e). The Cu₂O phase is characterized by a 2.0 V band gap with the valence-band maximum pinned at the Fermi level (\(E_F\)). This band arrangement identifies the material as p-type conductor and indicates the abundance of Cu-vacancies in the bulk lattice. [27] A pronounced kink at \(-0.25\) V in the \(dI/dV\) traces marks the bias position, at which the bulk position of the Cu₂O valence band is reached inside the crystallites. The bands of the Cu₃O₂ surface oxide are nearly symmetric with respect to the Fermi level. A pronounced peak at \(+0.75\) V inside the gap arises from the Au(111) surface state that is upshifted due to repulsive interactions with the dielectric film [37]. The different electronic properties of the two oxide phases give rise to variations in the optical response, as discussed next.

3. Results and discussion

3.1. Spectral analysis of the luminescence

We start our presentation with STM luminescence spectra of thick Cu₂O(111) patches and the Cu₃O₂ surface oxide (figures 2(a) and (b)). Both spectral series have been acquired as a function of bias with the CCD detector set to 30 s accumulation time \((I = 1.2\) nA). At first glance, the two data sets show similar behaviour, which indicates a strong involvement of the STM cavity in the emission process. The radiated intensity is focussed in a wavelength range from 700 to 800 nm with a shoulder at 870 nm, in clear contrast to the reported Cu₂O luminescence that exhibits an excited progression at 600 nm and defect-related peaks at 730 and 930 nm [31]. Despite their spectral similarity, the luminescence of thick and thin oxide patches can be distinguished by looking at the bias-dependence of the emitted intensity. To visualize the effect, the spectral series have been plotted in a wavelength-bias diagram with the intensity encoded in colour (figures 2(c) and (d)). The emission yield of thick Cu₂O patches hereby peaks at 2.0–2.5 V bias, while thin Cu₃O₂ is optically inactive in this range and exhibits an emission maximum at 5.3 V. Moreover, the total intensity is three times larger for Cu₂O than Cu₃O₂ oxide patches. A similar spectral response is revealed also at negative bias polarity; however, the unique bias dependence of the luminescence vanishes in this case. This observation gives a first hint at a deviating emission mechanism for the two oxide phases.

3.2. Elastic versus inelastic tunnelling channels

To gain further insights into the emission schemes, the \(dI/dV\) response of the two oxide phases is probed as a function of bias voltage and compared with the luminescence detected with the photomultiplier tube. The \(dI/dV\) signal hereby reflects the elastic tunnelling channel between tip and sample, while the optical response arises from an inelastic transport path [16, 18]. Three specific surface regions have been examined with the same tip configuration, namely a Cu₂O₂ area (panel (a)), a thin and a thick Cu₂O crystallite (panels (b) and (c)) (figure 3). The \(dI/dV\) traces of the surface oxide are dominated by the substrate and exhibit a low-lying resonance at 3.2 V due to the L-band edge in the Au(111) band structure, [38] and a series of field emission resonances (FERs) starting from 6.2 V [39]. The resonance behaviour in the \(dI/dV\) channel gets reproduced also in the tip-height, as every opening of a novel transport path causes the tip to retract from the surface to maintain the pre-set tunnelling current.

The \(dI/dV\) spectra of thick Cu₂O patches are clearly different (figure 3(c)). The peak at 3.2 V due to the L-edge has disappeared, while the FERs have shifted to lower bias, indicative for a work function decrease [40]. In addition, pronounced \(dI/dV\) intensity is detected between 2.0 and 4.0 V, reflecting the Cu₂O
Figure 2. STM luminescence spectra taken at different excitation bias on (a) thick Cu$_2$O and (b) thin Cu$_3$O$_2$. Tunneling current and CCD accumulation time were set to 1.2 nA and 30 s, respectively. Same data plotted in a wavelength-bias diagram to visualize the different bias positions of the emission maxima for (c) Cu$_2$O and (d) Cu$_3$O$_2$.

Figure 3. Constant-current $dI/dV$ spectra and relative tip heights (broken lines) measured on (a) the Cu$_3$O$_2$ surface oxide, (b) a thin and (c) a thick Cu$_2$O(111) patch. The simultaneously acquired luminescence yield is plotted in the second row. The surface positions for data acquisition are marked in the STM image shown in the inset (45 × 45 nm$^2$). (d) Similar data for negative bias polarity. As differences among the oxide regions are negligible here, only spectra for position (B) are displayed.

The $dI/dV$ signal can now be correlated to the simultaneously detected photomultiplier response. The pronounced intensity maximum at 5.3 V, as observed on the Cu$_3$O$_2$ surface oxide, coincides with the low-bias wing of the 1st FER. Conversely, the FERs produce only a moderate emission enhancement for thick Cu$_2$O patches. In fact, the maximum intensity is detected here at the conduction-band onset and quickly fades away at higher bias. As before, thin and thick Cu$_2$O crystallites show rather similar behaviour, suggesting that not the layer thickness but the different phase composition is behind the deviating emission response (figure 3(b)). At negative polarity, much smaller differences are discernible between the three surface regions, both in the conductance and the luminescence channel (figure 3(d)). The $dI/dV$ spectra are featureless apart from a small peak at $-4.0$ V, a behaviour that is reproduced in the optical curves. A discrimination of thin and thick oxide regions is neither possible in the $dI/dV$ nor the luminescence channel at negative polarity. In general, the bias-dependent luminescence measured with the photomultiplier tube closely follows the results of the spectral analysis discussed in section 3.1.
3.3. Spatial analysis of the luminescence

To complement the experimental section of this paper, spatial maps of the luminescence are presented together with the associated $dI/dV$ maps in the bias window from 1.8 to 5.3 V (figure 4). The corresponding topographic image shows large Cu$_2$O(111) patches covered with the characteristic ($\sqrt{3} \times \sqrt{3}$) R30° reconstruction, only interrupted by two triangular Cu$_3$O$_2$ regions. Inside the oxide band gap, both $dI/dV$ and luminescence channel exhibit low intensity. The situation changes first on thick Cu$_2$O patches, where photon and $dI/dV$ channel develop considerable intensity that peaks at $\sim 2.2$ V sample bias. The detected intensity evolution mimics the bias-dependent spectral courses discussed for the Cu$_2$O islands before. Surprisingly, electronic and optical maps in this bias range display a pronounced spatial inhomogeneity, most likely due to structural defects in the ($\sqrt{3} \times \sqrt{3}$) R30° reconstruction [33]. At intermediate bias, thin and thick copper oxide patches are nearly indistinguishable in the $dI/dV$ and optical channel. Clear contrast develops again at 5.3 V, when the Cu$_3$O$_2$ patches suddenly turn bright in the luminescence maps. The behaviour mimics the emission maximum that occurs when tunnelling in the low-bias wing of the 1st FER of the Cu$_3$O$_2$ surface oxide. The associated increase of the $dI/dV$ signal occurs at slightly higher bias and is not covered in this series.

3.4. Interpretation of the luminescence data

Using several experimental methods, we have demonstrated that thick bulk-type Cu$_2$O(111) patches and a thin Cu$_3$O$_2$ surface oxide have deviating luminescence properties, which enable discrimination of the two phases via photon mapping at the nanometre scale. Our finding is surprising at first glance, as the spectral signature of the emission is similar for both oxides and differences only occur in the bias-dependence of the radiated intensity. We will rationalize this behaviour by evaluating the interplay of plasmon-mediated light emission from the STM cavity and the electronic structure of the two oxide phases. For the sake of clarity, we start our discussion with the Cu$_3$O$_2$ surface oxide.

The luminescence from the Cu$_3$O$_2$ layer is safely assigned to plasmonic light emission, arising from electrodynamic coupling between the Au tip and sample across the tunnelling gap [16, 18]. Gold is a superior plasmonic material and light emission from an Au/Au junction is typically centred at 800 nm (1.5 eV), slightly red-shifted against the Mie resonance of an Au sphere representing the tip [41]. The luminescence detected here overlaps with this wavelength window, while its fine-structure is mainly governed by the microscopic tip shape and contains no information on the sample. The surface oxide itself is too thin to imprint its emission signature onto the spectra. This conclusion is supported by the polarity-independent nature of the low-bias luminescence, a clear sign for plasmon-mediated light emission driven by inelastic electron transport between tip and sample [16].

The observed emission maximum at 5.3 V, on the other hand, seems in conflict with a plasmon-mediated emission scheme and suggests a certain impact of the Cu$_3$O$_2$ spacer layer. In conventional metal/metal junctions, the luminescence typically peaks at about 2.5 V [18], when multiple inelastic transport channels are activated, while the low tip height still promotes plasmonic coupling between the two electrodes. In our experiments, only a weak photon signal is detected in this bias range, and the emission maximum occurs at voltages at which field-enhancement effects in the STM junction have already diminished. Apparently, plasmonic coupling alone cannot explain the bias dependence of the
emitted intensity. Detailed experiments on the role of the tip/sample distance on the emission yield are presented in the supplementary material (https://stacks.iop.org/NJP/23/093021/mmedia).

Besides field-enhancement effects, the stimulation of a plasmonic system depends also on the probability for inelastic energy losses of electrons on their way between tip and sample. Whereas tunnelling occurs at infinitively short times, electrons have finite residence times in the FERs given the classical nature of those states [39]. A finite lifetime, often associated with multiple reflections of the electron wave packets in the confining potential, now increases the probability for inelastic losses, hence for plasmonic excitations. In metal/metal junctions, the life-time effects in the FERs are not large enough to overcome the plasmonic field-enhancement at low bias, and the emission maximum remains at ∼2.5 V [42, 43]. In contrast, the intensity peak on Cu3O2 coincides with the bias position of the 1st FER (figure 5(a)). The deviating behaviour is explained with the dielectric nature of the surface oxide, the wavefunctions of which decay much faster towards the vacuum than on metal surfaces and consequently couple less efficiently to the FERs in the cavity. This gives rise to a barrier for electron propagation from the vacuum to the sample states, which increases the electron lifetime in the FERs and thus the probability for inelastic losses to the plasmonic system. Interestingly, the luminescence maximum on Cu3O2 does not exactly match the position of the 1st FER but locates at its low-bias wing (figure 3(a)). At this position, first electrons can reach the bound vacuum state, but the tip has not yet retracted from the surface and the plasmonic field enhancement remains high. Note that emission maxima located at the lower wing of a FER have been reported for ultrathin MgO/Mo(001) films before [25].

A different emission scheme is proposed for tip positions above bulk-type Cu2O(111) crystallites. At island heights of 1–3 nm, the plasmonic coupling between tip and Au(111) has already diminished, while the oxide itself does not support plasmonic modes on its own given the low free-carrier density. Pronounced optical activity is nonetheless detected at 2.0–2.5 V but drops off with increasing bias and only partly recovers in the region of the FERs (figure 3). Spectral analysis still confirms the plasmonic origin of the emission (figure 2), suggesting that the optical response of the two oxides differs only because of deviating pathways for plasmon stimulation. In a conventional metal/metal junction, even in presence of a dielectric spacer as the Cu3O2 discussed above, the plasmonic modes are stimulated by inelastic electron tunnelling from an initial tip state into a final sample state or vice versa [16, 18]. Loss energies are hereby governed by the spectral window of field-enhancement, being centred at ∼800 nm for the Au/Au cavity used here. This classical picture gets modified on top of the Cu2O crystallites, where at least one of the participating states needs to be situated in the oxide matrix. Wei hereby discard the option of initial and final state located in the tip and Cu2O valence band, respectively, as the bias-onset of the luminescence coincides perfectly with tunnelling into the oxide conduction band (figure 3(c)). In fact, inelastic tunnelling from the tip to the oxide valence states would be possible and even favourable below 2.0 V due to the blocked elastic channel, but was not observed in our study. Also, an initial state in the Cu2O conduction band and a final one in the Au(111) surface appears unlikely, as the hot electrons need to migrate through the entire Cu2O film and recombine at the metal/oxide interface in this case. Remains the third option, in which tip electrons get injected into the Cu2O conduction band and decay either directly or via defect-induced gap states to the valence band by exciting the gap plasmons (figure 5(b)).
Two questions immediately arise in connection with the proposed mechanism: (i) What is the nature of empty states in the oxide valence band and (ii) why is the Cu$_2$O band recombination with its unique excitonic signature not seen in the luminescence data? The first question was already addressed in earlier work [44]. In short, our Cu$_2$O films have pronounced p-type character with a finite hole concentration in the valence band. At positive sample bias, the holes migrate to the surface in response to the tip-electric field, where they accumulate in an empty-state pocket above $E_F$ (figure 5(b)). These empty valence states are clearly detected as $dI/dV$ peak in the band gap (figure 1(e)), [44] and provide the final states for electron recombination from the conduction band. The expected excitonic signature of band recombination, on the other hand, is covered by the much stronger plasmon modes of the STM cavity. Plasmon-mediated decay occurs on fs-time scales, hence much faster than the assembly and recombination of an electron/hole pair. In addition, direct gap transitions and the decay of the $n = 1$ exciton are dipole-forbidden in Cu$_2$O for parity reasons [20, 31]. The electron transition between conduction and valence band thus stimulates plasmonic instead of excitonic light, in contrast to molecular systems with strong, dipole-allowed excitonic modes [14, 15]. Our model also explains why the highest emission yield is observed at 2.2 V and decays afterwards. With rising bias, high-lying conduction states get populated in the Cu$_2$O islands but cannot recombine with the empty valence-band pocket because the released energy quantum lies outside the field-enhancement window of the Au/Au junction (700–900 nm, figure 2). Thermalization of the hot electrons to the band bottom, on the other hand, competes with their field-driven migration to the Cu$_2$O/Au(111) interface, impeding a radiative transition into the empty valence pocket at the surface. Both arguments are in line with the observed maximum of the Cu$_2$O(111) emission at 2.0–2.5 V sample bias.

4. Conclusions

STM luminescence spectroscopy offers a reliable pathway to distinguish Cu$_2$O and Cu$_3$O$_2$ oxide patches on Au(111) with nanometre spatial resolution. Although the spectral signature of the luminescence is similar in both cases, indicative for a predominantly plasmonic origin, its unique bias dependence enables clear distinction of the two oxide phases. The light emission from the Cu$_3$O$_2$ surface oxide is governed by inelastic energy losses of electrons in the 1st FER to the plasmonic system of the STM cavity and peaks at 5.3 V. On bulk-type Cu$_2$O(111) islands, on the other hand, electron transitions between the oxide conduction band and valence band are the stimulus for plasmon excitations. The latter scheme is particularly effective at ~2.2 V sample bias, when electrons get injected into the bottom of the oxide conduction band and tip-induced band-bending effects are small. Our experiments demonstrate the dominance of plasmonic with respect to excitonic light emission from an STM junction, even in presence of a thick and optically active dielectric layer. To probe the excitonic response of oxides, two strategies are proposed for the future. First, the oxide films will be thickened beyond present values, which might be challenging due to their insulating nature. And second, gold needs to be replaced with a non-plasmonic tip material in order to strengthen excitonic with respect to plasmonic recombination channels in the STM cavity.

Supplementary material contains information on the spatial resolution achieved in the photon mapping, on the emission yield as a function of the tip-sample distance and on the role of the tip material in the luminescence process.

Acknowledgments

We thank C Noguera and J Goniakowski for their vital role in clarifying the structure of the copper oxide films. Financial support from the DFG Grant Ni 650-5 ‘towards an atomic-scale understanding of ideal, defective and doped cuprous oxide surfaces and interfaces’ is gratefully acknowledged.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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References

[1] Weiner A 2009 Ultrastat Optics: Principles and Techniques (New York: Wiley)
[2] Jupille J and Thornton G 2015 Defects at Oxide Surfaces (Berlin: Springer)
[3] Häkansson U, Johansson M K-J, Holm M, Pryor C, Samuelson L, Seifert W and Pistol M-E 2002 Appl. Phys. Lett. 81 4443
[4] Myrach P, Nilius N and Freund H J 2011 Phys. Rev. B 83 035416
[5] Esmann M et al 2019 Nat. Nanotechnol. 14 698
[6] Qi X H, Nazin G V and Ho W 2003 Science 299 542
[7] Doppiagne B, Chong M C, Lorchat E, Berciaud S, Romeo M, Bulou H, Boeglin A, Scheurer F and Schull G 2017 Phys. Rev. Lett. 118 127401
[8] Benia H-M, Myrach P, Gonchar A, Risse T, Nilius N and Freund H J 2010 Phys. Rev. B 81 241415
[9] Liu S, Müller M, Sun Y, Hamada I, Hammad A, Wolf M and Kumagai T 2019 Nano Lett. 19 5725
[10] Krane N, Lotze C, Läger J M, Reecht G and Franke K J 2016 Nano Lett. 16 5163
[11] Pommier D et al 2019 Phys. Rev. Lett. 123 027402
[12] Dong Z C, Guo X L, Trifonov A S, Dorozhkin P S, Miki K, Kimura K, Yokoyama S and Mashiko S 2004 Phys. Rev. Lett. 92 086801
[13] Schultz J F, Li S, Jiang S and Jiang N 2020 J. Phys.: Condens. Matter. 32 463001
[14] Imada H, Miwa K, Imai-Imada M, Kawahara S, Kimura K and Kim Y 2017 Phys. Rev. Lett. 119 013901
[15] Merino P, Roslawksa A, Große C, Leon C C, Kuhnke K and Kern K 2018 Sci. Adv. 4 eaap8349
[16] Johansson P, Monreal R and Apell P 1990 Phys. Rev. B 42 9210
[17] Urbiet a M, Barby M, Zhang Y, Koval P, Sánchez-Portal D, Zahala N and Aizpurua J 2018 ACS Nano 12 585
[18] Berndt R, Gimzewski J K and Johansson P 1991 Phys. Rev. Lett. 67 3796
[19] Liu S, Wolf M and Kumagai T 2018 Phys. Rev. Lett. 121 226802
[20] Meyer B K et al 2004 Phys. Status Solidi 241 231
[21] Stankic S, Müller M, Diwald O, Sterrer M, Knözinger E and Bernardi J 2005 Angew. Chem., Int. Ed. 44 4917
[22] Likovich E M, Jaramillo R, Russell K J, Ramanathan S and Narayanamurutti V 2011 Appl. Phys. Lett. 99 131910
[23] Stavale F, Nilius N and Freund H-J 2013 J. Phys. Chem. Lett. 4 5972
[24] Fernández I, Cremades A and Piqueras J 2005 Semicond. Sci. Technol. 20 239
[25] Benia H M, Myrach P and Nilius N 2008 New J. Phys. 10 013010
[26] Stavale F, Nilius N and Freund H-J 2012 New J. Phys. 14 033006
[27] Meyer B K et al 2012 Phys. Status Solidi B 249 1487
[28] Thewes J, Heckötter J, Kazimierczuk T, Aßmann M, Föhlich D, Mayer B, Semina M A and Glazov M M 2015 Phys. Rev. Lett. 115 027402
[29] Weiner J S, Caswell N, Yu P Y and Mysyrowicz A 1983 Solid State Commun. 46 105
[30] Snoke D W, Shields A J and Cardona M 1992 Phys. Rev. B 45 11693
[31] Ito T and Masumi T 1997 J. Phys. Soc. Japan 66 2185
[32] Musa A O, Akomolafe T and Carter M J 1998 Sol. Energy Mater. Sol. Cells 51 305
[33] Gloystein A and Nilius N 2020 J. Phys. Chem. C 124 28605
[34] Gloystein A, Nilius N, Goniatkowski J and Noguera C 2015 J. Phys. Chem. C 124 26937
[35] Möller C, Fedderwitz H, Noguera C, Goniatkowski J and Nilius N 2018 Phys. Chem. Chem. Phys. 20 5636
[36] Schulz K H and Cox D F 1991 Phys. Rev. B 43 1610
[37] Gloystein A and Nilius N 2019 J. Phys. Chem. C 123 26939
[38] Pan Y, Benedetti S, Nilius N and Freund H J 2011 Phys. Rev. B 84 075456
[39] Becker R S, Golovchenko J A and Swartzentruber B S 1985 Phys. Rev. Lett. 55 987
[40] Rienks E D L, Nilius N, Rust H-P and Freund H-J 2005 Phys. Rev. B 71 241404
[41] Schull G, Becker M and Berndt R 2008 Phys. Rev. Lett. 101 136801
[42] Berndt R and Gimzewski J K 1993 Ann. Phys. 305 133
[43] Martinez-Blanco J and Fölsch S 2015 J. Phys.: Condens. Matter. 27 255008
[44] Gloystein A and Nilius N 2021 Phys. Status Solidi B 2100337