Microscopic Heterogeneities in the Electrical Properties of SiC as Studied with Single-Molecule Spectroscopy

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We report on electric-field-tuning experiments of single chromophores in a transparent matrix on top of a microcrystalline layer of silicon carbide (SiC). Upon changes of the electric field strength, most single-molecule lines show a slow creeping behavior toward a new equilibrium position. We attribute the relaxations to slow charge rearrangements in the SiC on a (sub)microscopic scale. This interpretation is supported by atomic force and scanning electron microscopy images of the SiC surface, which show mosaic structures with a typical grain size of about 300 nm.

Introduction

Silicon carbide (SiC), which is an indirect-gap semiconductor, has several outstanding properties as compared to other semiconductor materials such as silicon, gallium arsenide, or indium phosphide. Its band gap is almost three times as large as that of silicon. The thermal conductivity is over three times that of silicon and almost 10 times that of gallium arsenide and indium phosphide. SiC has the ability to operate at very high temperatures up to 700 °C. These physical properties could make semiconductor devices possible that operate at much higher voltages and current densities with reduced cooling requirements. Growing single crystals of SiC is very difficult, however. It was suggested that SiC could replace silicon in high-power applications, provided that the problems of crystal growth can be overcome.[1] Crystalline SiC has also a number of remarkable mechanical and chemical properties. It is almost as hard as diamond (Mohs hardness 9.3) and is therefore widely used for passivation and protective layers. Its corrosion resistance is outstanding. Below 1000 °C, it is only corroded by melts of oxides.[2] SiC exists in more than 200 polytypes.[3] Whereas all of them have very similar mechanical and thermal properties, their electrical and optical characteristics can vary considerably. Protective layers of SiC are usually fabricated by physical vapor transport (PVT).

The spectroscopy of single chromophore molecules embedded in a solid matrix[4−6] has proven to be a promising tool for investigating solid-state properties on a nanometer scale. At liquid-helium temperatures, the zero-phonon lines of polycyclic aromatic dye molecules in several matrices have widths of only $10−100$ MHz. This allows one to employ single chromophore molecules as highly sensitive probes for their local nanoenvironments. Internal processes or external forces, which shift the resonance frequency of a single molecule on the order of 10^{-7} of the absolute optical frequency, are easily detectable. An important application[7] of single-molecule spectroscopy (SMS) has been the study of low-energy excitations (two-level systems, TLSs), which are present in all glasses and also in crystalline

materials. Their exact physical nature is not known for most materials. Yet, it is believed that they are due to collective movements of groups of atoms or molecules between two metastable configurations. Flips between these two states change the surrounding strain field and, in this way, cause the resonance frequency of adjacent chromophore molecules to shift instantaneously.

An external electric field changes the spectral position of an atomic or molecular transition by

$$\Delta\nu_{\rm E} = -\frac{1}{h}\left(\kappa\vec{\mu}\cdot\vec{E} + \frac{1}{2}\kappa^2\vec{E}\tilde{\alpha}\vec{E}\right) \tag{1}$$

where $\vec{\mu}$ is the difference between the dipole moment vectors and $\tilde{\alpha}$ the difference between the tensors of electrical polarizability between the excited and ground state of the system. $\vec{E}$ is the (macroscopic) electrical field strength and $\kappa = (\epsilon + 2)/3$ the local field correction factor. Centrosymmetric molecules such as terrylene and pentacene exhibit only a quadratic Stark effect in a vacuum, but when embedded in a solid matrix, they usually gain permanent dipole moments due to distortions by the surrounding matrix. This leads to an additional linear contribution to the Stark shift, which, at moderate field strengths, is usually much stronger than the quadratic shift.

Experimental Section

In the present paper, we report on electric-field measurements of single-molecule lines, where the chromophores were embedded in a Shpol'skiĭ or polymeric matrix on a SiC substrate. The chromophores were highly diluted so that in the focus there was no more than one chromophore molecule in resonance with the exciting laser light. The substrates (provided by the Fraunhofer-Institut für Mikroelektrische Systeme und Schaltungen, Munich, Germany) were interdigitating gold electrodes on a glass chip; they had distances of 10, 18, or 50 μm and a thickness of 300 nm and were covered with a 500-nm-thick protective layer of SiC. The small spacing of the electrodes permits the generation of high electric field strengths with moderate voltages. The SiC layer was deposited by plasma-enhanced chemical vapor deposition.

In the case of the polymer matrix polyisobutylene (PIB), the samples were prepared by spin-coating a mixed solution of tetra-

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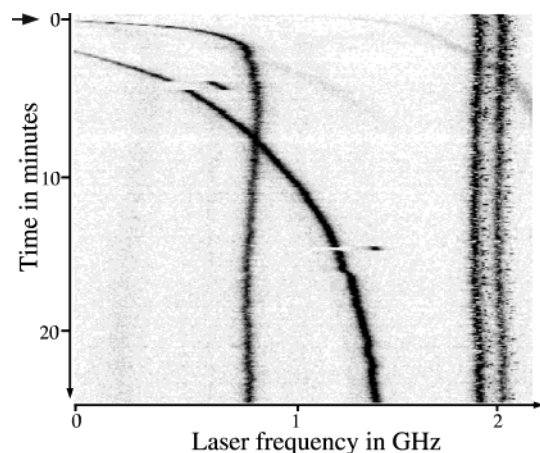† Email address: lothar.kador@uni-bayreuth.de.
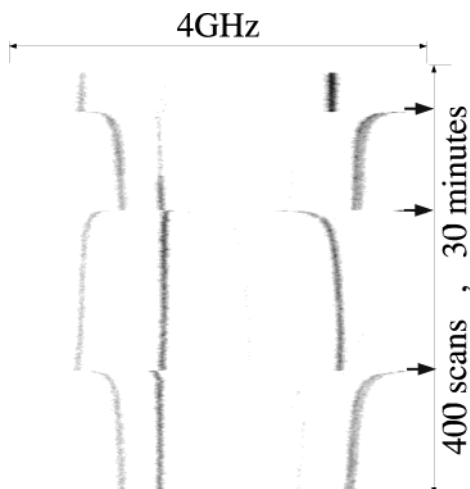
Figure 1. Temporal creeping of the resonances of single terrylene molecules in *n*-hexadecane toward new equilibrium positions after fast changes of the external field strength. The points in time when the electric field was switched between ±15 kV/cm are indicated by arrows. Two different types of relaxation are observed.

Figure 2. Part of a spectral trace containing the lines of three DBATT molecules. Two of them show relaxation of type II with different time constants. The electric field was switched only once at time zero.

Figure 3. Spectral trace of a single terrylene molecule (a) showing relaxation behavior of type I and (b) the final relaxation (after switching the field strength back to zero) in more detail. The solid line is a biexponential fit to the data.

tert-butyl-terrylene (TBT) and PIB in toluene onto the electrode chip. Shpol'skiĭ samples were prepared by placing a small drop of *n*-hexadecane premixed with a polycyclic aromatic chromophore suitable for SMS (terrylene, DBATT, or 2.3,7.8-di-(peri-naphthylen)-pyren) onto the chip. The latter molecule is a new dye for SMS, which, in *n*-hexadecane, has similar properties as the commonly used terrylene but absorbs at slightly longer wavelengths. A microscope cover glass was placed on the sample solution, so typical thicknesses of the samples of a few micrometers were achieved.

Fluorescence excitation spectra were recorded with a frequency-stabilized single-mode dye laser COHERENT CR599-21. The excitation wavelength was in the range 565−585 nm. The laser beam was directed into a ^{4}He cryostat and focused to a diffraction-limited spot with a microscope objective (60×, NA = 0.85). The sample was immersed in superfluid helium below 2 K. The fluorescence was collected with the same objective in confocal configuration and detected with a single-photon counting avalanche photodiode module. In the experiments, we repeatedly tuned the laser over a range of a few gigahertz and constructed spectral trails from the data. Each scan consisted of 1000 or 2000 points and was completed in 4−10 s. After a few dozen scans, the voltage applied to the electrodes (a few volts) was switched stepwise between different values.

Results and Discussion

The usual behavior of single-molecule lines upon sudden changes of the electric field strength is that their resonance frequencies jump immediately to the new values. In striking contrast, molecules on the electrode chips with the SiC layer exhibit a slow temporal creeping of the resonance frequency, which we had already described in a previous paper[8] and which will be discussed in more detail in the following. Figure 1 shows the spectral trails of three terrylene molecules in *n*-hexadecane. The time traces are depicted from top to bottom in the images (except of Figure 3). The fluorescence intensity is encoded on a gray scale with dark shades corresponding to high signal amplitudes. The points in time at which the electric field strength was switched (here between +15 and −15 kV/cm) are indicated by arrows. The continuous spectral creeping occurs on a time scale of a few minutes.
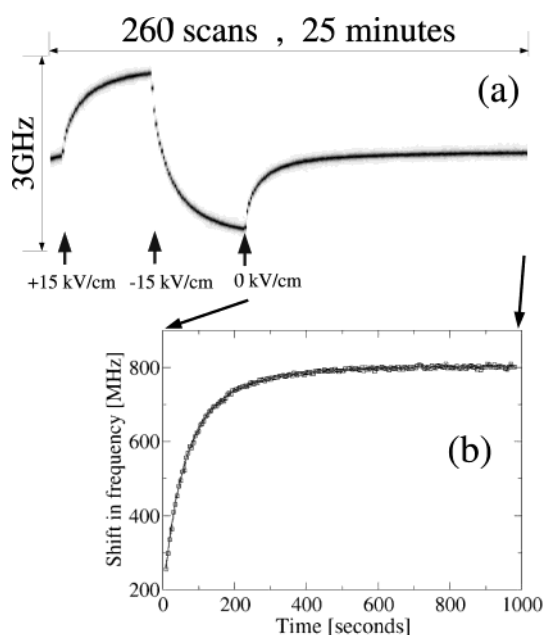
The molecules exhibit spectral creeping of two different types. Part of them move slowly (sometimes after a small initial jump) from their previous frequency position toward the new equilibrium value; this behavior will be denoted as type I. Other single-molecule lines perform a sudden jump and then relax in the opposite direction (behavior of type II). Molecules of both types could be found in the same focal spot (see the left and right resonance in Figure 1). On the other hand, the prevailing behavior was found to slightly change with the location on the sample.

Figure 2 shows another example of resonances of single DBATT molecules in *n*-hexadecane. Here the electric field was switched only once by 12 kV/cm at the top of the diagram at time zero. The two DBATT lines on the left-hand side exhibit relaxation of type II yet with strongly different time constants. The fast moving resonance even reverses the direction of its relaxation around the time 5 min.

Figure 3a shows a terrylene molecule with behavior I in more detail. In this example, the electric field was switched from zero to +15 kV/cm, then to −15 kV/cm, and finally back to zero.

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The time traces are here depicted from left to right. Figure 3b shows the frequency position of the line maximum as obtained by Lorentz fits to the spectra. The figure shows the data from the moment when the voltage was switched back to zero (indicated by arrows). The solid line in Figure 3b is a biexponential fit. In this example, the two exponentials have time constants of 40 and 140 s and relative amplitudes of 1 and 0.5, respectively. Fits with a single-exponential, a stretched-exponential, or a logarithmic function were, in general, not satisfactory. This is immediately evident for one of the resonances in Figure 2, which changes its creeping direction.

We investigated a few hundred single-molecule resonances in *n*-hexadecane and PIB on the electrode chips with the SiC passivation layer. Virtually all of them showed the temporal creeping behavior of either type I or II. The creeping was absent only for those chromophores of which the dipole moment difference in the direction of the external field was zero and which, consequently, did not show any linear Stark shift (see, for example, the resonance on the right-hand side of Figure 2, which is split into two components due to the interaction with a fast flipping TLS). The overall amplitudes of the Stark shift were similar to literature data.[9] A detailed comparison of the matrix-induced dipole moments was not possible, however, since the results depend strongly on the measurement time and the experimental details because of the creeping.

We carefully checked that the temporal relaxation is not an experimental artifact. The contacts to the electrodes were of low resistance, so the charging time was well below a millisecond. Moreover, slow charging of the electrodes would always result in a monoexponential line shift of type I with identical time constant for all molecules. In the experiments, however, we observed relaxation of both types with different time constants even for molecules in the same focal spot. We can also rule out heating effects due to electrical currents as the source of the spectral shifts. The resistance between the electrode arrays was very high, and the resulting surface current density in the sample (current divided by the edge length of the electrodes) was below 10^{-8} A/cm in all cases. This upper limit was measured close to the breakdown voltage of the electrodes in the superfluid helium.

Spectral shifts of type II can, in principle, be explained by relaxation of TLSs, which carry electric dipole moments. After a change of the external field, groups of atoms can slowly relax or reorient themselves so as to screen the field. Such a behavior was already observed in hole-burning experiments[10,11] in PMMA as the origin of the temporal evolution of the hole width after a sudden change of the field strength. Figure 4 shows the spectral trail of a single terrylene molecule, the resonance frequency of which jumps repeatedly in the direction of the previous equilibrium position (highlighted by ellipses). These jumps are very likely due to field-induced flips of a TLS. In a hole-burning experiment, where an ensemble of molecules is probed, this behavior would lead to a narrowing of the hole spectrum after the initial broadening. Figure 4 demonstrates that field-induced jumps of TLSs occur also in Shpol'skiĭ matrixes. We observed field-induced spectral jumps only very rarely, however. Furthermore, it is unlikely that the smooth creeping behavior, which most single-molecule resonances in our experiments show, is due to TLS relaxation. The TLS density in a polycrystalline alcane matrix is far too low to account for a continuous motion on the frequency axis. Only a few TLSs in the immediate neighborhood of a dye molecule can cause large frequency shifts, which are then expected to consist of few discrete jumps.
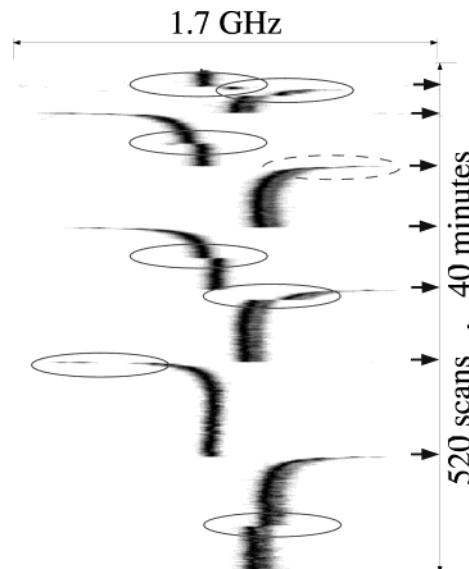
Figure 4. Spectral trace of a single terrylene molecule showing relaxation behavior of type II and field-induced flips of one TLS (highlighted by ellipses).

The relaxation behavior of type I cannot be understood in terms of TLS relaxation at all.

In some of our experiments, we used electrode chips without a SiC layer. In none of these cases was the creeping observed. It did not occur either when the SiC was covered with a layer of SiO or undoped polyisobutylene (PIB) prior to sample deposition. Also in experiments with custom-made aluminum electrodes,[12] we did not observe temporal creeping of single-molecule resonances. When a very thin layer (~100 nm) of PIB doped with TBT molecules was spin-coated directly on the SiC, only part of the TBT lines exhibited the creeping behavior. Thus the temporal creeping of single-molecule resonances is clearly connected with the SiC layer. In the measurements with *n*-hexadecane, the matrix is a few micrometers thick. The nonpolar chromophores, however, tend to be located very close to the substrate surface.[13] In the polymer matrix, the accumulation at the surface seems to be less pronounced or absent. Covering the SiC with an insulating layer of SiO or undoped PIB prevents close contact of the chromophores with the SiC, and the creeping disappears. The fact that both type I and type II and different time constants are present in the same focal spot of about 0.5 μm diameter indicates that the mechanism in the SiC that causes the creeping must vary roughly on the length scale of the focal spot size (or slightly smaller).

We inspected the SiC layer on the electrode chips with an atomic-force microscope (AFM) and a scanning-electron microscope (SEM). Figure 5a shows an AFM image of the surface topography in an area of 2 μm side length. The full contrast corresponds to topographic height variations of about 5 nm. The observed features are partly smoothed and broadened by the scanning tip. A SEM image of a fracture of the SiC layer is shown in Figure 5b. The horizontal axis spans again 2 μm. With both techniques, a pattern of structures of about 300 nm size is visible, which probably represent microcrystallites or regions of different polytypes. This seems reasonable, since the SiC passivation is not grown epitaxially on the electrode chip.

The structures in the SiC layer of submicrometer size lead us to propose a mechanism of the spectral creeping, which is sketched in Figure 6. Regions of different electrical conductivity in the SiC (for instance, crystallites and boundaries between
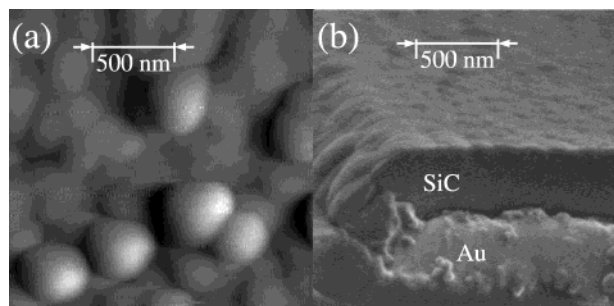
Figure 5. Atomic force microscopy image (a) of the SiC passivation layer and (b) scanning electron microscopy image of a fracture of the electrode chip.
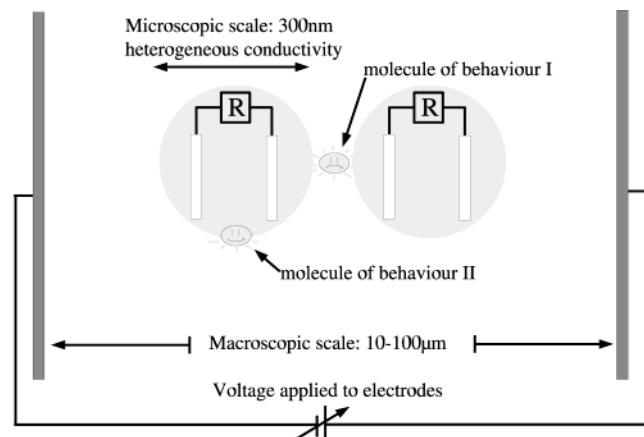
Figure 6. Sketch of the proposed mechanism in the SiC causing the temporal creeping behavior.

them) form small capacitive elements, which can be located in the neighborhood of dye molecules close to the SiC surface. In this picture, the creeping of single-molecule lines after a fast switch of the external field is due to redistributions of charges on the microscopic capacitors with time constants $\tau = RC$. The local electric field at the position of the dye molecule can then increase or decrease with time. For a dye molecule that is located between two capacitor plates with a conductive connection, the external field is increasingly shielded after a voltage switch, which results in a creeping behavior of type II (molecule on the left side in Figure 6). If there are regions of decreasing field strength, there must also be areas in which the field increases with time, since the integral over the field strength (i.e., the applied voltage) is constant. Positions of increasing field strength can be located between capacitive elements (see the molecule in the center of Figure 6). In this picture, it is also clear that molecules in the same focus will tend to have the same relaxation time, as they are under the influence of mainly the same capacitive element. This was indeed observed experimentally in the majority of the measurements (e.g., see Figure 1, where even resonances with opposite creeping behavior have within errors the same relaxation time). Yet, an example to show the opposite is Figure 2, where the resonances have strikingly different relaxation times. Also the nonexponential time dependence can be understood within this model. The local field strength felt by a dye molecule is mainly affected by the redistribution of charges on nearby capacitive elements. The time constants $\tau = RC$ of different elements are expected to be different, since they depend on the details of their microscopic structures. The superposition of different charging times will then yield the observed nonexponential behavior. The fast moving resonance in Figure 2, which slightly reverses its creeping direction after a few minutes, can also be understood

in this way. This molecule seems to occupy a site where it feels the influence of (mainly) two capacitive elements, one causing the fast shielding or attenuation of the external field (behavior of type II) and another one with a much smaller contribution to the relaxation behavior of type I from a more distant capacitive element with a long time constant. We expect that the time constants vary over several orders of magnitude. Our experimental data, however, are only affected by charge redistributions occurring between about 1 s and a few minutes. The structural size of the pattern seen in the AFM and SEM images is also in agreement with our observation that the prevailing relaxation behavior varies slightly with the position of the focal spot on the electrode chip. We speculate that the regions of higher conductivity are probably located at grain boundaries, where many defects are present. Inside the grains, the material is expected to be crystalline and highly insulating. In the sketch of Figure 6, a single crystallite of SiC would then comprise the central region with the two inner capacitor surfaces, whereas the outer plates would be located on neighboring grains.

It is instructive to estimate the resistance R in the proposed microscopic circuits. If we assume a typical size d of 300 nm for a capacitor (both extension and distance of the plates), its resulting capacitance $C = \epsilon\epsilon_0 d^2/d$ is on the order of 10^{-17} F (for $\epsilon \approx 6$). Our observed time constants $\tau = RC$ then correspond to resistance values between 10^{17} and 10^{19} Ω. They are huge and are in accordance with the very high macroscopic resistance of SiC, which renders the material suitable for passivation and applications as an insulator. We can only detect these resistance values because local variations of the conductivity lead to the tiny capacitances. If the conductivity were homogeneous and of the same order of magnitude, it would be completely undetectable even with single-molecule spectroscopy.

Most experiments in single-molecule spectroscopy have so far been used to study properties of the chromophores themselves or of the surrounding organic host matrix. Caruge and Orrit have demonstrated that local inhomogeneities of the current flow in a semiconducting substrate can strongly influence the spectroscopic characteristics of single dye molecules.[13] The present work is another example that single chromophores can be employed as local probes for their micro- and nanoenvironment and that they can even detect inhomogeneities of a substrate. The sensitivity of single molecules to local electric or strain fields and to variations of the local temperature or currents is unsurpassed and presents the ultimate limit of spatial and spectral selectivity. The relative positions of single fluorescing chromophores can be determined to an accuraccy that far exceeds the usual resolution limit of optical far-field techniques.[14,15] In this way, one can also envisage, for example, experiments on the surfaces of superconductors, phase-separated materials, or solid-state devices.

Conclusion

In summary, we have performed electric-field measurements on single-molecule resonances, when the samples were located on electrode chips covered with a SiC passivation layer. Upon fast switching of the external field, almost all chromophores showed a slow spectral creeping behavior, the time dependence of which was nonexponential in most cases. The effects were similar for different dyes and for a Shpol'skiǐ and a polymer matrix. The time constant(s) and the type of creeping varied from molecule to molecule, even within the same focal spot. We could rule out field-induced TLS flips as the origin of the peculiar temporal creeping. Instead we presented a phenom-

enological model, which is based on strong local variations of the electrical conductivity in the SiC layer. According to this model, the continuous slow spectral shifts of single-molecule lines are due to redistributions of charge carriers on a submicrometer length scale within times between seconds and many minutes. Simple estimates show that extremely high local electrical resistances can be determined in this way.

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