

Communications

Highly Anisotropically Self-Assembled Structures of *para*-Sexiphenyl Grown by Hot-Wall Epitaxy**

By Andrei Andreev, Gebhart Matt, Christoph J. Brabec,*
Helmut Sitter, Dirk Badt, Heinz Seyringer, and
N. S. Sariciftci

Research on conjugated polymers and oligomers is a rapidly expanding field within materials science due to the promising opportunities for applications of these π -electron semiconductors in electronics and photonics. Conjugated polymers combine properties of classical semiconductors with the inherent processing advantages of plastics and therefore play a major role in low-cost, large-area optoelectronic applications. On the other hand the interest in oligomers comes from the well-defined chemical structure and a defect-free, highly ordered structure in the solid state in contrast to the disordered phases of the polymers. π -Conjugated oligomers such as oligothiophenes or oligophenylenes have been successfully used as active layers in field effect transistors (FETs)^[1] and light-emitting diodes (LEDs).^[2] These molecules are thermally stable up to 300–400 °C, can be obtained as pure materials (up to electronic grade), and can be processed as thin films in high vacuum or ultrahigh vacuum conditions. The morphology, molecular packing, and structural properties of these thin films are essential for their optical properties and charge transport through the active layer.^[3]

The present work focuses on *para*-sexiphenyl (PSP), a six units oligomer of *para*-phenylene. PSP is a promising candidate as an electroactive layer in organic colored LED dis-

plays^[4] due to its blue luminescence with high quantum yield.^[2c] The luminescence and the optical absorption of the PSP films are polarized along the long axis of the molecules. Thus, the macroscopic anisotropy of the absorption and emission strongly depends on the relative orientation of the molecules on the substrate.^[5,6] In this report we show that, depending on the growth conditions, anisotropic films of crystalline PSP with dichroic ratios up to 14 in emission can be produced.

Sexiphenyl crystallizes monoclinic,^[7,8] in a space group $P2_1/c$, with lattice constants of $a = 8.091 \text{ \AA}$, $b = 5.568 \text{ \AA}$, $c = 26.241 \text{ \AA}$ and monoclinic angle of $\beta = 98.17^\circ$. The positions of the atoms in the unit cell are known from single-crystal investigations:^[8] the molecular axes are parallel for all molecules in the lattice and the planes of the molecules have two different angles of inclination with respect to the surface normal in adjacent layers. The molecular axes are not parallel to the c -axis but slightly inclined relative to it. The X-ray reflections (the 2θ value for $\text{Cu K}\alpha$ radiation) for sexiphenyl were calculated and experimentally tested elsewhere.^[9a]

Thin films of PSP are traditionally grown by physical vapor deposition.^[5,6,9] It was shown that the substrate temperature during evaporation and the deposition rate are important parameters for molecular packing in the solid-state structure. In particular, the films deposited on GaAs, glass, indium tin oxide (ITO) coated glass, or KCl at high substrate temperatures demonstrate preferred growth in the (001) orientation with the molecules aligned roughly perpendicular to the substrate.^[5,6,9] At low substrate temperatures, preferred growth in the (11 $\bar{2}$) and (20 $\bar{3}$) orientations develops and the layers consist dominantly of molecules whose long axes are preferentially inclined parallel to the substrate.^[5,9] Generally, the films grown by vapor deposition consist of randomly oriented islands whose shapes and structures depend on the purity of the source material and on growth conditions.^[9a]

Recently, Müller et. al.^[10] reported that large islands of PSP (several micrometers long, about 1 μm wide), which are well-defined and oriented into two perpendicular twin directions, can be obtained at similar growth conditions as reported in the literature^[9] on GaAs(001) substrates using molecular beam epitaxy (MBE). This report demonstrated the influence of a suitable growth technique on the quality of structured thin films of oligomers.

In this communication we report on the application of a comparable simple technique promising for the growth of conjugated oligomers, namely hot-wall epitaxy (HWE),^[11,12] to produce highly ordered thin films of PSP with high crystallinity at the macroscopic scale. In contrast to the deposition methods discussed above, HWE allows the growth of

[*] Dr. C. J. Brabec, Dr. A. Andreev,^[+] G. Matt, Dr. N. S. Sariciftci
Christian Doppler Laboratory for Plastic Solar Cells
and Institute for Physical Chemistry
J. Kepler University Linz
Altenbergerstr. 69, A-4040 Linz (Austria)
Prof. H. Sitter, H. Seyringer
Institute for Semiconductor and Solid-State Physics
J. Kepler University Linz
Altenbergerstr. 69, A-4040 Linz (Austria)
Dr. D. Badt
Institute for Biophysics
J. Kepler University Linz
Altenbergerstr. 69, A-4040 Linz (Austria)

[+] Permanent address: Institute for Physics of Microstructures RAS,
GSP-105, 603600 Nizhny Novgorod, Russia.

[**] The Austrian Foundation for Advancement of Scientific Research (FWF project number P-12680-CHE) and the European Commission (Joule III Program, grant JOR3-CT98-0206) are acknowledged for financial support. Part of this work was performed within the Christian Doppler Foundation's dedicated Laboratory for Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs and Quantum Solar Energy Linz Ges. m. b. H.

epitaxial layers close to thermodynamic equilibrium^[13,14] and as a consequence the large organic molecules can find the most suitable arrangement before being incorporated into the crystal lattice, resulting in highly ordered structures of the deposited layers. Hence, HWE growth of PSP on well-defined crystalline surfaces is interesting not only in terms of device applications but also in terms of the fundamentals of epitaxial growth. In this context, we selected as a convenient substrate material freshly cleaved mica, because the extremely small surface roughness of this substrate does not mask the intrinsic features of the film. The mica is already well known to be a good substrate for the growth of C₆₀^[11,12] and sexithienyl (T6)^[15] epitaxial layers with remarkably high crystalline quality. All our samples were grown at a substrate temperature of 90 °C where preferential orientation of the molecules is expected.^[9]

The crystalline structure and the orientation of our PSP films were determined by X-ray diffraction (XRD) measurements. Only a (11 $\bar{1}$) reflection from the film and (00 l) reflections from the mica substrate were observed in $\theta/2\theta$ scans. Hence, from XRD one can conclude that the HWE technique yields highly crystalline PSP films oriented along (11 $\bar{1}$). This is similar to results obtained for PSP films grown at low substrate temperatures on GaAs.^[9] For this type of growth the angle between the long axis of the sexiphenyl molecules and the substrate surface is rather small, resulting in “lying” molecules.^[9a]

Figure 1a shows an atomic force microscopy (AFM) image of the surface morphology of a typical PSP film grown by HWE on mica within one hour. In contrast to T6 thin films on mica^[15] and PSP films on GaAs^[9,10] grown by other techniques, a long-range ordered structure with a strongly

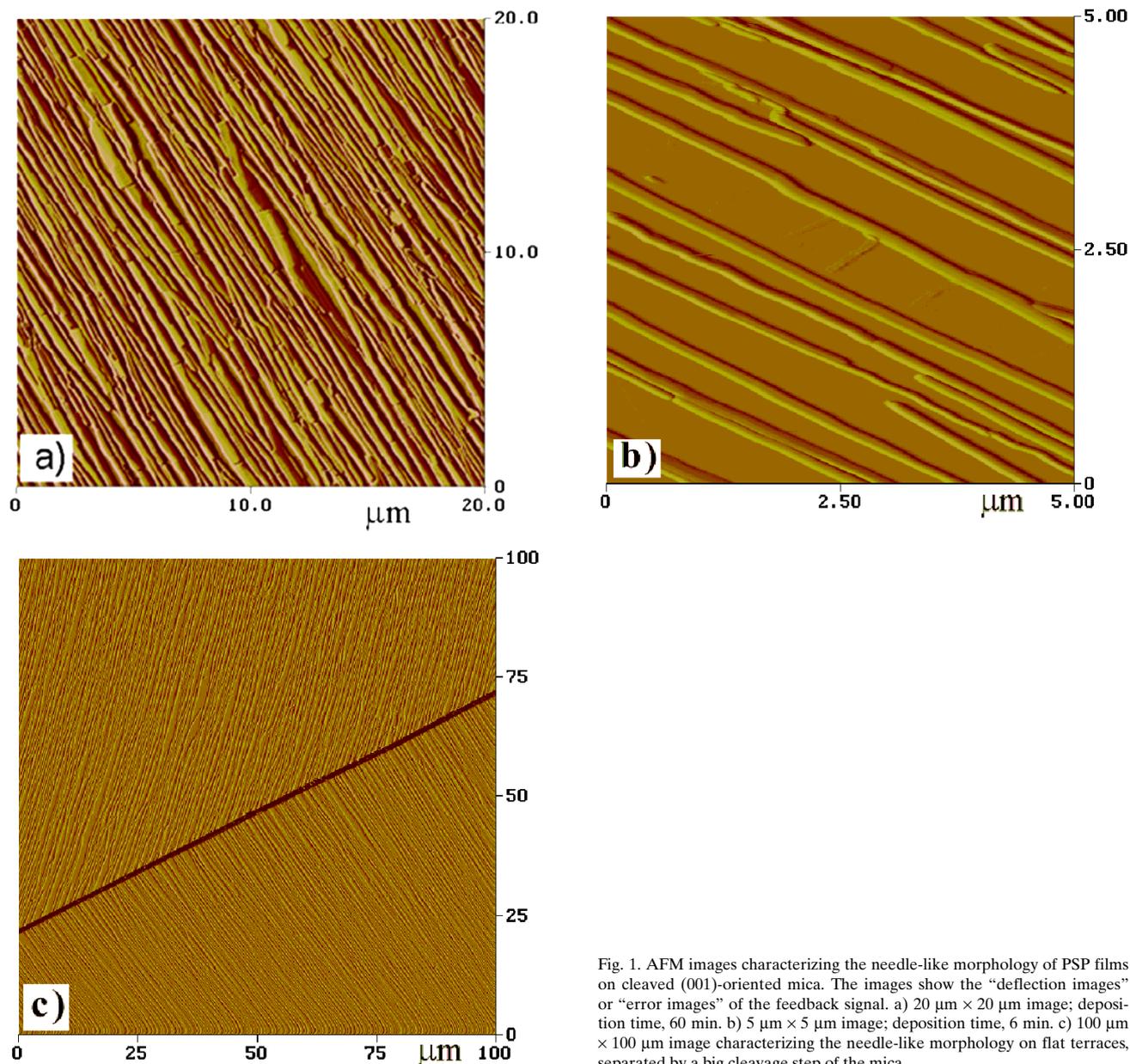


Fig. 1. AFM images characterizing the needle-like morphology of PSP films on cleaved (001)-oriented mica. The images show the “deflection images” or “error images” of the feedback signal. a) 20 μm × 20 μm image; deposition time, 60 min. b) 5 μm × 5 μm image; deposition time, 6 min. c) 100 μm × 100 μm image characterizing the needle-like morphology on flat terraces, separated by a big cleavage step of the mica.

expressed preferential direction is observed. This structure consists of large oriented crystallites looking like very long “needles”, which are parallel to each other and separated by relatively flat areas. AFM line profile measurements show that the “needles” depicted in Figure 1a are typically about 130 nm high and up to 800 nm wide with flat areas of 300–400 nm in between. “Needles” with a length of up to $\approx 100 \mu\text{m}$ were detected, showing a length-to-width ratio of the order of 100. Hence the “needles” (crystallites) are strongly anisotropic and their axes align along one preferential direction. Such a needle-like structure can be observed at a growth time as short as a few minutes, as depicted in Figure 1b, i.e., for thin films of PSP. Here the “needles” are smaller but again up to $\approx 100 \mu\text{m}$ long (length-to-width ratio of the order of 500) and the preferential direction is more pronounced due to the shorter growth time. On perfectly cleaved mica this preferential direction does not change over the entire film surface of $\sim 20 \text{ mm}^2$, as found by light microscopy studies. On mica terraces, separated by big cleavage steps, the preferential direction of the “needles” can change by 120° from terrace to terrace, while the morphology of the “needles” remains identical. A typical example is shown in Figure 1c. The turnaround of the “needles” by 120° seems to be based on an interaction between the deposited PSP molecules and the different layers of mica.^[16] The roughness of the space between the needles is determined to be 3–4 nm, which is comparable to the roughness on the “surface” of the “needles” ($\approx 3 \text{ nm}$). Cleaved mica typically shows a surface roughness around 0.2–0.3 nm. Therefore, we assume that the PSP films are closed and the areas between the “needles” are also covered by sexiphenyl.

According to XRD and AFM data the PSP films grown by HWE on mica are highly anisotropic and, consequently, one would expect to see high dichroic ratios in the absorption and emission of light. In Figure 2 the polarized UV-vis absorption spectrum of a film (its morphology is depicted in Fig. 1a) is shown for different angles of the polarizer with respect to the “needles”. The plotted curves show a well-pronounced maximum around 366 nm for the polarizer perpendicular to the “needles”. For the excitation beam polarized parallel to the “needles”, no significant absorption band can be observed within the experimentally accessible window down to 300 nm. The maximum centered at $\approx 366 \text{ nm}$ becomes tilted when the angle between the direction of the “needles” and the electric field vector of the exciting light is close to 0° . At 366 nm we observe a dichroic absorption ratio between parallel and perpendicular polarization of more than 11. It was shown earlier that the optical absorbance of PSP films depends strongly on the orientation of the sexiphenyl molecules relative to the substrate/incident beam: the absorption parallel to the chain is characterized by a peak at about 380 nm and perpendicular to the chain by an absorption band around 280 nm.^[6] We therefore conclude that the dominant peak at $\approx 366 \text{ nm}$, observed for the polarization perpendicular to the “needles”,

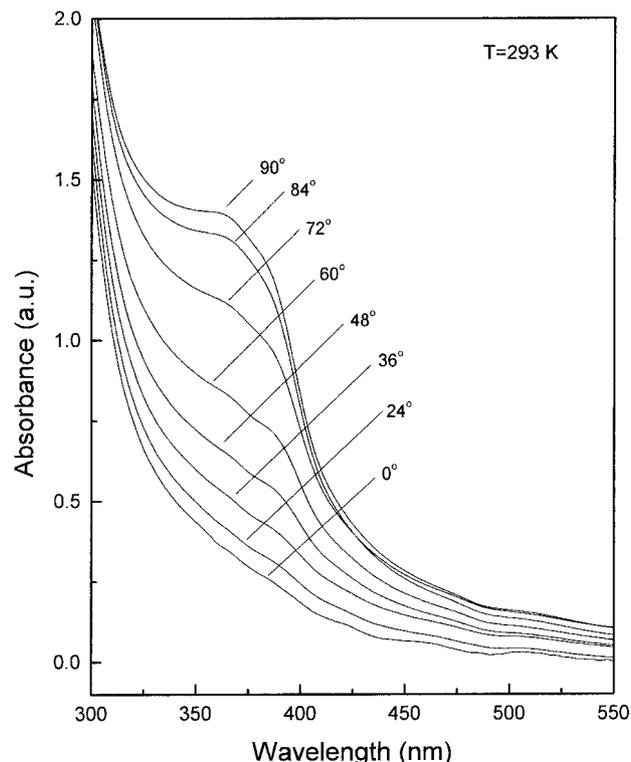


Fig. 2. Angularly resolved polarized UV-vis absorption spectra of a PSP film (normal incidence). Angle of field relative to needles: 0° , field parallel to the direction of the “needles”; 90° , field perpendicular to the direction of the “needles”.

is due to the π - π^* absorption of molecules that are slightly tilted towards the substrate surface with their long axes almost perpendicular to the “needle” axis.^[6] This is in agreement with our XRD studies presented above and implies a very well ordered stacking of PSP molecules.

IR spectroscopy provides information on the molecular basis and is a powerful tool for studying the alignment of single molecules in oriented, thin organic films.^[17] The polarization-dependent IR reflection spectra shown in Figure 3 confirm the alignment of the PSP molecules perpendicular to the “needles”. We concentrate the discussion on three vibrational bands: according to the analysis of Louarn et al., the bands at 760 and 815 cm^{-1} are assigned to the C–H out-of-plane bending vibration on mono- and para-substituted phenyl rings, respectively,^[18,19] while the band at 1479 cm^{-1} is assigned to the ring stretching vibration along the molecular axis.^[18] The intensity of the C–H bands (vibration polarized perpendicular to the long axis of the molecules) can be tuned between 0 and 100 % by changing the angle between the needles and the electric field vector. The ring stretching band (vibration polarized along the molecular axis) shows the opposite dependence on the polarization. The intensities of bands show a strong cosine-type dependence on the angle (see Fig. 3, inset). This behavior can only be understood if the PSP molecules are mostly arranged with their long axes perpendicular to the “needles”, showing only a small inclination towards the substrate surface.

One of the applications to be developed in the near future is polarized LEDs. Obviously, a necessary condition for polarized electroluminescence is polarized photoluminescence. In order to determine the polarization degree of the light emitted from these highly ordered PSP films, we performed photoluminescence (PL) measurements in a two polarizer geometry for the pump polarization and probe polarization (Fig. 4, left, inset). Typical photoluminescence spectra are shown in Figure 4. For all four permutations of polarizations a well-known PL spectrum (upper spectrum) with three pronounced bands^[18–20] is observed. The PL emission shows vibronic fine structure.^[18] The maximum of emission is observed again if the excitation acts perpendicular to the direction of the “needles”, consistent with both UV-vis absorption and IR reflection data. The dichroic ratio for 90°–90° emission compared to 0°–0° is ≈14. The strong emission bands have the electric field vector component perpendicular to the film surface, indicating that the PSP molecules are aligned not absolutely flat on the substrate, but are tilted slightly out of plane. From our optical experiments it is very difficult to derive an exact value for the inclination angle between the molecular axis of the PSP molecules and the substrate plane.

The driving force for spontaneous formation of the large, well-ordered “needle” structures could come from anisotropic elastic strain induced by the lattice mismatch. Such phenomena should be more clear expressed at thermodynamic equilibrium condition because in this case the molecules can find the energetically optimal place more easily before being incorporated into the crystal lattice. Note that, in contrast to HWE, the growth process by flash evaporation or by MBE of oligomers runs very far from equilibrium.

In summary, thin films of *para*-sexiphenyl with optical dichroic ratios of up to 14 were grown on cleaved mica substrates using the HWE technique. The films are crystalline and oriented along (11̄). Self-organization of PSP molecules occurs during HWE growth, resulting in long-range ordered needle-like structures with a strongly expressed preferential direction, and a length-to-width ratio of up to 500. According to all optical and XRD data, the PSP molecules are basically lying on the substrate at a small tilt angle to the surface and with their long axes almost perpendicular to the direction of the “needles”. The potential of HWE for the growth of highly ordered structures, as demonstrated in

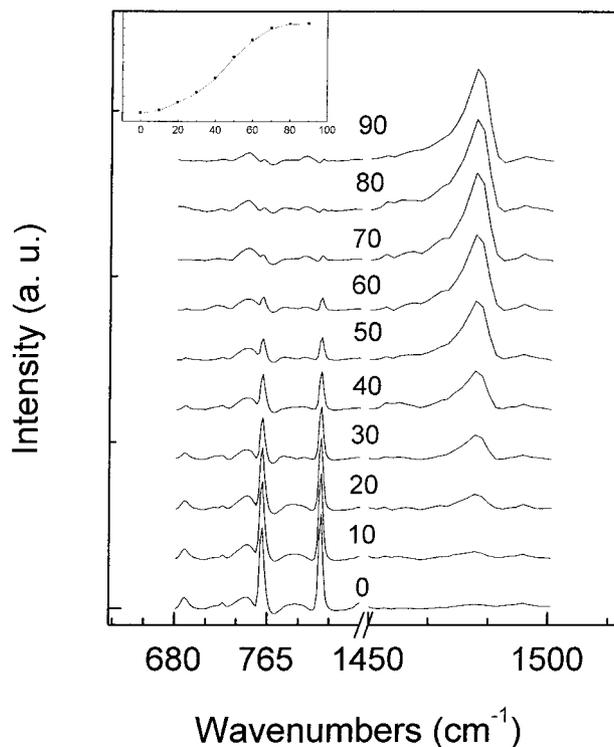


Fig. 3. Angularly resolved polarized IR reflection spectra of a PSP/mica film. Angle of field relative to needles: 0°, field parallel to the direction of the “needles”; 90°, field perpendicular to the direction of the “needles”. Inset: the angular dependence of the 1479 cm⁻¹ vibration.

this work, has interesting implications in terms of polarized optoelectronic devices based on conjugated oligomers.

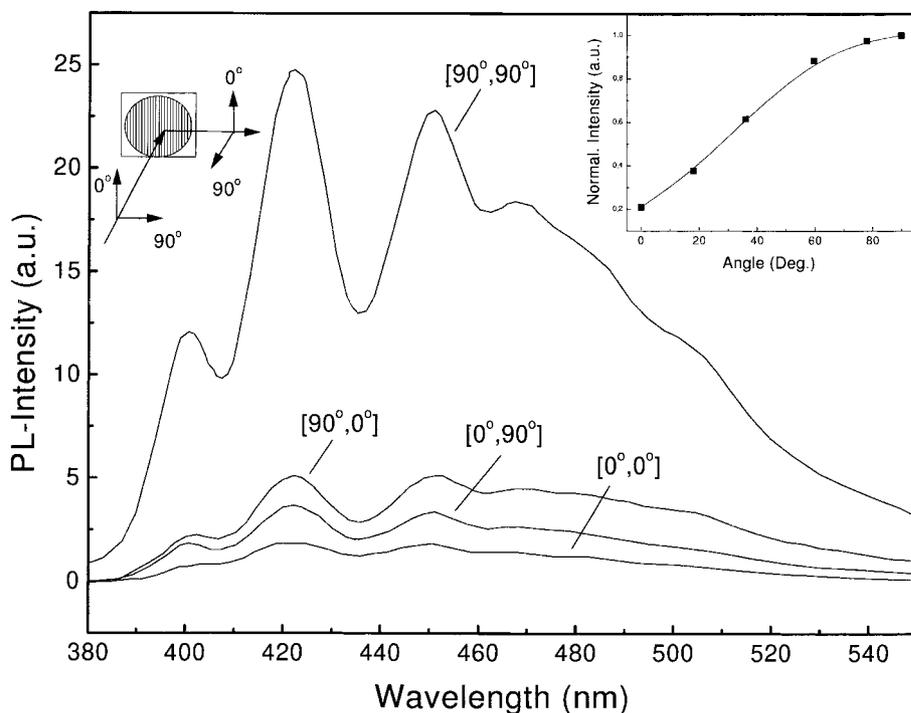


Fig. 4. Polarized PL spectra of a PSP film at room temperature for excitation at 350 nm. Inset, left: a schematic representation of measuring geometry. Inset, right: the angular dependence of the emission for excitation polarized at 90°.

Experimental

Materials: High-purity *para*-sexiphenyl (PSP) powder was purchased from TCI-GR Co., Japan. Further purification was performed by threefold sublimation at 280 °C under a dynamical vacuum of 1×10^{-6} mbar. The substrate used was freshly cleaved (001)-oriented Muscovite mica.

Growth of PSP: Thin films were grown in a HWE system, which has been used previously for the successful deposition of high-quality crystalline films of C₆₀ and Ba₆C₆₀ [11,12]. In the growth chamber of the system a HWE reactor and a preheating/annealing oven were installed. The reactor consisted of two separately heated ovens for the wall and source zone, which could be kept at different suitable temperatures during growth. The quartz tube with the source material at the bottom was mounted inside the oven. The substrate was placed close to the tube end and could be heated separately. The hot wall zone between the substrate and the source guaranteed a nearly uniform and isotropic flux intensity and high kinetic energy of the molecules. The sample holder could be moved from the preheating oven to the HWE reactor and back using a computer-controlled step-motor. The vacuum during growth was about 6×10^{-6} mbar. All films were grown at a constant substrate and source temperature of 90 °C and 240 °C, respectively. The wall temperature was in the range of 240–260 °C. These growth parameters resulted in a low deposition rate of about 2 nm/min, which gave nominally ≈120 nm thick films within the typical deposition time of one hour.

AFM Measurements: The film morphology was investigated by AFM with a NanoScope IIIa (Digital Instruments, Santa Barbara, CA) operated in contact mode in air.

XRD Measurements: The crystalline quality of the PSP films was investigated using a conventional X-ray diffractometer in coupled $\theta/2\theta$ reflection mode using Cu K α radiation.

Optical Characterization: All measurements were performed at room temperature. Polarized absorption spectra were recorded with an UV-vis HP spectrophotometer at normal incidence. Polarized photoluminescence spectra were measured on a Hitachi F-4010 fluorescence spectrometer at normal incidence. Infrared reflection measurements were performed using a Bruker IFS-66 FTIR spectrometer.

Received: November 8, 1999

Final version: February 21, 2000

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Electron Transport Properties of Nanocrystals: Isolated, and "Supra"-Crystalline Phases

By Abdelhafed Taleb, Fabian Silly, Alexander O. Gusev, Fabrice Charra, and Marie-Paule Pileni*

Single electron tunneling on nanometer-sized metals is recognized as the fundamental concept for ultimate miniaturization in microelectronics.^[1] In recent years, a new class of electronic devices—single electron tunneling transistors—has been obtained.^[2,3] This is a result of the considerable progress achieved in imaging, measuring and manipulating material properties down to the atomic length scale.

Scanning tunneling microscopy (STM) is an indispensable tool for exploring phenomena down to the atomic level. This is primarily based on the ability to obtain local information on electronic,^[4,5] chemical,^[5,6] and optical properties.^[7–9] A rather large number of groups have investigated electrical properties of nanocrystals deposited on substrates with various coatings,^[2–16] results indicating that these are promising candidates for future nanoscaled architecture in microelectronic technology.

For an isolated metallic object of capacitance C , the energy associated with the transfer of one electron from a tip to the particle is $E_c = e^2/2C$, where e is the elementary charge unit. The system composed of a tip and a metallic particle deposited on the substrate is equivalent to two tunnel junctions coupled in series. One (adjustable) tunnel junction is formed between the STM tip and the metal particle. A second fixed junction exists between this particle and a conducting substrate. Coulomb blockades with and without staircases were previously observed at room temperature.^[17,18]

* Prof. M.-P. Pileni, Dr. A. Taleb
Laboratoire S.R.S.I., U.R.A. C.N.R.S. 1662
Université P. et M. Curie BP 52
4 place Jussieu, F-75005 Paris (France)
Dr. F. Silly, Dr. A. O. Gusev, Dr. F. Charra
C.E.A.-C.E.N. Saclay
Service de Recherche sur les Surfaces et l'Irradiation de la Matière
F-91191 Gif-sur-Yvette Cedex (France)