

Optimized preparation of cross-sectional TEM specimens of organic thin films

A.C. Dürr^{a,*}, F. Schreiber^{a,b,1}, M. Kelsch^a, H. Dosch^{a,b}

^a *Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany*

^b *Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany*

Abstract

We present a route for the preparation of cross-sectional TEM specimens of crystalline organic thin films which minimizes the mechanical, chemical and thermal load of the organic film during preparation and allows to take TEM images with molecular resolution. A typical example of a thin film of diindenoperylene capped with a thin layer of gold is shown to demonstrate the application of the technique for the investigation of metal–organic interfaces.

© 2003 Elsevier B.V. All rights reserved.

PACS: 06.60.c; 68.37; 81.07.b; 81.65.Ps

Keywords: Cross-sectional transmission electron microscopy; Sample preparation; Diindenoperylene; Organic thin films; Metal–organic interfaces

1. Introduction

Thin films of organic semiconductors are expected to play a significant role in future organic electronic devices. Besides the intrinsic properties of the materials involved the structural quality has a great impact on the performance of such devices as has the quality of the interface between metal-contacts and the organic layer. These structural issues are usually investigated by various experimental methods, such as AFM, STM, SEM, LEED, and X-ray-scattering [1].

Cross-sectional transmission electron microscopy (TEM) is a very powerful tool for the study of real-space structures including defects and interfaces with resolution down to the atomic scale. Whereas cross-sectional TEM-characterization with high resolution (several Å) of crystalline *inorganic* samples is well-established in material science, it is only rarely used for crystalline *organic* samples (see, for example, Refs. [2–4]). This is mainly due to (a) the delicate preparation of TEM specimens, (b) the weak contrast of organic materials (mostly C-atoms and H-atoms), and (c) the potentially limited stability of organic films in the electron beam.

The preparation of cross-sectional TEM specimens is usually done by fabricating a sandwich structure and subsequently thinning this sandwich structure until it becomes transparent for electrons (thickness of the order of 100 nm, depending on

*Corresponding author. Tel.: +49-(0)711-689-1846; fax: +49-(0)711-689-1902.

E-mail addresses: arndt.duerr@mf.mpg.de (A.C. Dürr), kelsch@mf.mpg.de (M. Kelsch).

¹New address: Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England.

the specific absorption of the sample). This procedure is time-consuming and includes gluing of the specimen, baking in an oven, and the application of organic solvents such as acetone which potentially jeopardizes the stability of organic thin films. However, it allows for the best control during preparation and is very reproducible. Another method is to cut a thin slice of the sample with an ultramicrotome knife and subsequently thin this slice until it becomes electron-transparent [2,5,6]. Also, cleaving of thin samples is used to produce TEM specimens with a minimum of mechanical and chemical treatment (in this case, the substrate is thinned to only several μm prior to deposition of the organic thin film) [3].

For the investigation of the in-plane structure of organic thin films, the preparation of specimens in *transmission* geometry is reported, for example, in Ref. [7]. Here, the film is prepared on substrates like NaCl, which are finally dissolved in water so that only the organic thin film is left for the analysis in the TEM.

All the above preparation routes generally require a certain level of experience even for comparatively stable inorganic samples. If applied to potentially less stable organic thin films, additional care is required. In fact, one may take the view that the difficulties in preparation are the main reason for the limited use of TEM in this area.

In this paper we outline our procedure for the preparation of cross-sectional TEM specimens of organic thin films showing high crystalline order

which allows the observation of individual lattice planes of the organic film with molecular resolution. Thin films of diindenoperylene (DIP) are used as an example. These films are capped by layers of thermally evaporated Au which makes it an interesting system to study interdiffusion being a technologically important issue for organic–inorganic interfaces [5,6,8].

2. Sample preparation and characterization

Thin films of DIP ($\text{C}_{32}\text{H}_{16}$, see right-hand side of Fig. 1) with a thickness of $D_{\text{DIP}} \approx 400 \text{ \AA}$ were prepared on thermally oxidized (4000 \AA) Si(1 0 0) substrates at a substrate temperature of $145 \pm 5^\circ\text{C}$ and at a deposition rate of $12 \pm 3 \text{ \AA}/\text{min}$ under UHV-conditions (base-pressure better than $5 \times 10^{-10} \text{ mbar}$).

Films prepared under these conditions exhibit high crystalline order normal to the surface with mosaicities of $< 0.02^\circ$ as probed by X-ray diffraction (see Figs. 2(a) and (b)). The molecules are essentially standing upright with a vertical lattice spacing of $d_{\text{DIP}} = 16.56 \text{ \AA}$. In addition, the DIP-films are closed, crystalline across their entire thickness, and they exhibit large terraces (extending up to several 100 nm) as confirmed by non-contact AFM measurements [10,11]. These well-defined surfaces in combination with the high crystalline order make DIP-films ideally suited as an organic model system to study the interfacial morphology of metal contacts on top of organic thin films. Thus, thin layers of gold ($D_{\text{Au}} \approx 120 \text{ \AA}$)

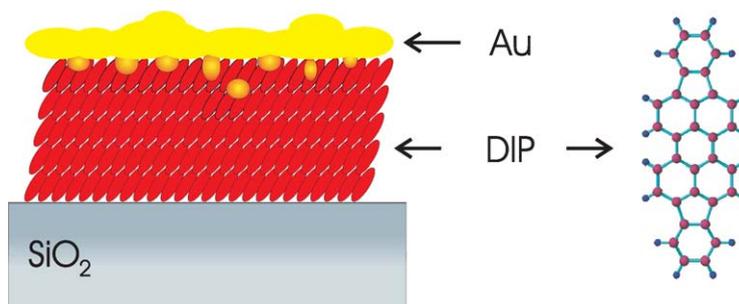


Fig. 1. Schematic of the sample structure (left-hand side): the Au-film is deposited on top of the essentially upright standing DIP molecules. Depending on the conditions during Au deposition the degree of Au diffusion into the organic layer is expected to vary [4,9]. On the right-hand side, the structure of a DIP molecule ($\text{C}_{32}\text{H}_{16}$) is displayed.

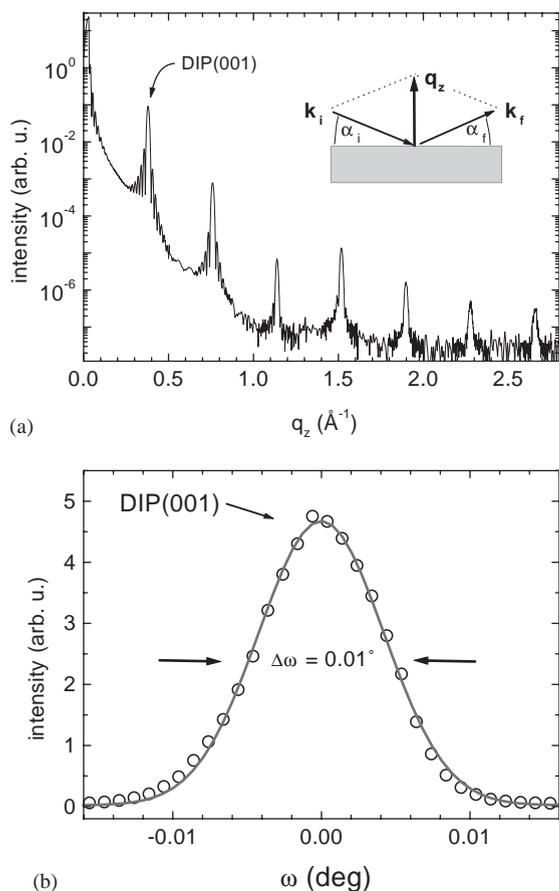


Fig. 2. (a) Specular X-ray scan of a DIP-film with $D_{\text{DIP}} = 385 \text{ \AA}$. Seven Bragg reflections associated with the DIP film demonstrate the high crystalline order of the DIP molecules normal to the substrate surface. Details about the crystallinity of DIP-films can be found in Ref. [10]. The inset sketches the scattering geometry. (b) Rocking scan over the DIP(001) reflection with a FWHM as small as $0.010 \pm 0.0003^\circ$.

were deposited onto the DIP-films under various deposition conditions [4,9]. The left-hand side of Fig. 1 sketches a microscopic view of the sample structure.

3. Preparation of cross-sectional TEM specimens

All samples investigated by cross-sectional TEM were prepared in the following way using particular care to minimize mechanical and thermal

exposure of the sensitive organic layer:

1. A small slice of the sample (width $\leq 2 \text{ mm}$) is cleaved into two pieces. Cleaving the sample prevents damaging of the original sample surface which may occur by sawing the sample.
2. The two pieces are glued together without using a brush to disperse the glue over the surface. Subsequently, the glue (*Gatan GI*) is stabilized in an oven at $T = 70^\circ\text{C}$ for 2 h resulting in a sandwich consisting of the layers Si/SiO₂/DIP/Au/glue/Au/DIP/SiO₂/Si. Note, that we use considerably lower temperatures and longer times than usually employed for the *Gatan GI* glue (stabilizing at $T = 130^\circ\text{C}$ for 30 min).
3. The sandwich is fixed in a copper tube with 3 mm outer diameter and 2 mm inner diameter (see Fig. 3). This is necessary to mechanically stabilize the sandwich structure which otherwise could disintegrate due to the weak bonding of the organic thin film at the substrate.
4. The copper tube is sliced with a diamond wire saw into thin slices of about 500 μm thickness.
5. The thin slices are ground and polished on one side, subsequently turned over and then ground to a final thickness of $\approx 80 \mu\text{m}$.

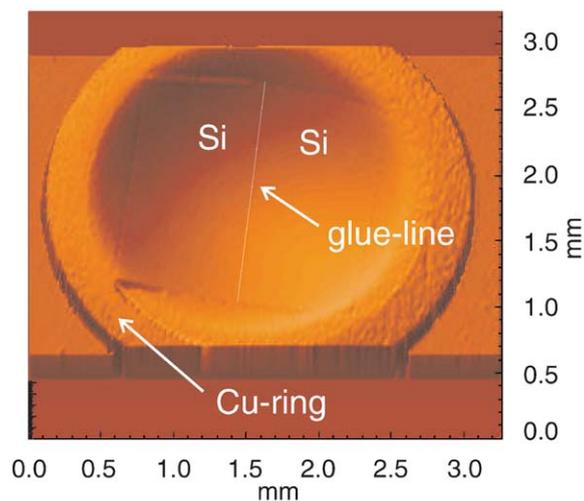


Fig. 3. 3D-profile of a prepared TEM specimen just before insertion into the ion-mill. The glue-line (indicated as white line) is the center of the sandwich-structure and contains the parts SiO₂/DIP/Au/glue/Au/DIP/SiO₂.

6. The simply ground side of the specimen is dimple-ground and polished to a thickness of $\leq 15 \mu\text{m}$ which is indicated in the present case of a Si-substrate by dark red transparency (see Fig. 3 for a 3D-specimen profile after step 6).
7. The specimen is thinned in an ion-mill under persistent liquid nitrogen (LN_2) cooling until a hole has formed in the center—at this point the edges of the hole are transparent for electrons (thickness: 10–100 nm). The ion-mill is operated at 4 kV, 1 mA, and at an incident angle of the argon-ions of 13° in the double sector thinning mode.

While the above preparation route is essentially standard for inorganic systems, its application to organic systems requires special care.

In step 2, it is particularly important to use an epoxy-glue which stabilizes at comparatively low temperatures ($T \ll 100^\circ\text{C}$) in a short time in order to minimize the time the organic film is exposed to elevated temperatures.

Grinding and polishing the thin slice in step 5 implies fixing the specimen onto a sample holder with a thin layer of wax (for each side once). After the polishing procedure, the wax has to be removed with acetone. In this step one has to take care that (a) the specimen is fixed quickly onto the sample holder which is kept at $T \approx 130^\circ\text{C}$ in order to melt the wax and that (b) the amount of acetone used to remove the wax is minimized since acetone may dissolve the organic film.

Finally it is preferable to cool the specimen during the ion-milling process (step 7), again, to minimize thermal exposure of the organic film.

Note, that also the choice of the substrate has to be considered carefully. Extremely hard substrates (e.g., sapphire) require a long grinding-process until their thickness is reduced sufficiently. Since the duration of the mechanical treatment also should be kept to a minimum, less hard substrates such as silicon are preferable.

With the above described procedure we successfully prepared cross-sectional TEM specimens of several different Au/DIP-structures. Usually, several TEM specimens were prepared from a single Au/DIP-sample since only 30–50% of them gave reasonable images.

4. Typical results

With the above described TEM-preparation high-resolution cross-sectional TEM images can be taken on the Au/DIP heterostructures, a schematic of which is depicted in Fig. 1. TEM images were taken with two different instruments, a CM200 microscope (Philips) operated at 200 keV and a JEM 4000 FX microscope (JEOL) operated at 400 keV, respectively. The point-resolution was 2.7 \AA (CM200) and 2.0 \AA (JEM 4000 FX), respectively. The samples remained stable in the electron beam for 1–2 min, sufficient for taking representative images of the interface

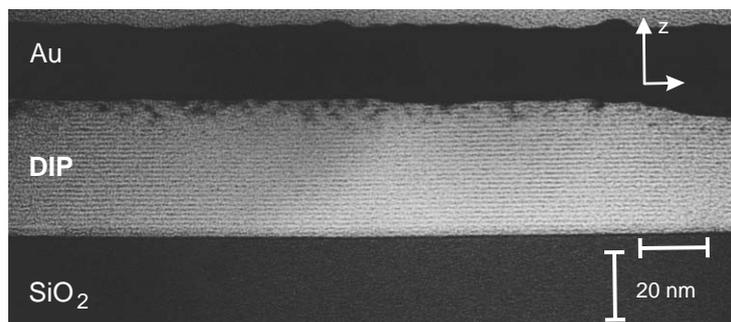


Fig. 4. Cross-sectional TEM-image of a heterostructure Au/DIP/SiO₂. One can clearly distinguish individual monolayers of the DIP-film as pairs of bright-dark contrast. The Au/DIP interface is well-defined with only some small clusters of gold-atoms diffused into the topmost layers of the DIP-film (dark features underneath the Au/DIP interface).

(the exposure time for the photographs was 1...3 s). Note that the stability of the samples was larger by a factor of ≈ 2.5 in the JEM 4000 FX microscope compared to the CM200 which may be due to the smaller inelastic scattering cross-section at higher energies. The stability may be increased in further experiments by cooling the specimen to LN₂-temperature.

As shown in Fig. 4, individual monolayers of DIP are well-resolved in the TEM-images as pairs of bright-dark contrast. At this point we note that the high crystalline order (as evidenced by the X-ray measurements, Fig. 2) and the small mosaicity of the DIP lattice planes are helpful for the resolution of individual monolayers by TEM.

With the TEM-images it is possible to study the quality of metal–organic interfaces immediately after metal deposition. Moreover, the degree of metal diffusion into the organic layer, i.e., the depth of diffusion and the size of the metal-clusters can easily be evaluated [4,9]. In the present case of Au deposited on a DIP-film (Fig. 4) only a negligible amount of diffusion of Au-clusters into the DIP-layer is found. Here, the Au-film was deposited at low sample temperature ($T = -120^\circ\text{C}$) and at a high deposition rate ($R = 20 \text{ \AA}/\text{min}$). In this case the diffusion of Au into the DIP-film is restricted to a range of about 100 Å. The typical size of the Au-clusters as derived from the image is $\lesssim 3 \text{ nm}$.

5. Conclusions

Although the preparation of specimens for cross-sectional TEM is delicate, TEM can clearly contribute a wealth of information also for organic thin films.

Using the specimen preparation scheme as outlined in the present paper we could take high-resolution TEM images of crystalline organic thin films with molecular resolution and a stability in

the beam of the order of 1–2 min. The obtained molecular resolution is even more remarkable given that the compound under investigation does not contain any heavy elements. Besides the preparation described here, other methods, e.g., employing an ultramicrotome knife or cleaving the sample structure have been reported in literature [2,5] and may also be optimized for the application to organics.

Acknowledgements

We wish to thank B. Struth and O. Konovalov at the ESRF, Grenoble, France, for excellent technical support during the X-ray studies, and N. Karl and S. Hirschmann for purification of the DIP-molecules by gradient sublimation. FS acknowledges support from the DFG within the focus program “Organische Feldeffekt-Transistoren”.

References

- [1] S.R. Forrest, Chem. Rev. 97 (1997) 1793.
- [2] J. Takada, Jpn. J. Appl. Phys. 34 (1995) 3864.
- [3] G. Philipp, C. Müller-Schwanneke, M. Burghard, S. Roth, K. von Klitzing, J. Appl. Phys. 85 (1999) 3374.
- [4] A.C. Dürr, F. Schreiber, M. Kelsch, H.D. Carstanjen, H. Dosch, Adv. Mater. 14 (2002) 961.
- [5] F. Faupel, Adv. Mater. 2 (1990) 266.
- [6] F. Faupel, R. Willecke, A. Thran, Mater. Sci. Eng. R22 (1998) 1.
- [7] A. Hoshino, S. Isoda, T. Kobayashi, J. Cryst. Growth 115 (1991) 826.
- [8] R. Weber, K.-M. Zimmermann, M. Tolan, J. Stettner, W. Press, O.H. Seeck, J. Erichsen, V. Zaporozhchenko, T. Strunskus, F. Faupel, Phys. Rev. E 64 (2001) 061508.
- [9] A.C. Dürr, F. Schreiber, M. Kelsch, H.D. Carstanjen, H. Dosch, O.H. Seeck, J. Appl. Phys. 93 (2003) 5201.
- [10] A.C. Dürr, F. Schreiber, M. Münch, N. Karl, B. Krause, V. Kruppa, H. Dosch, Appl. Phys. Lett. 81 (2002) 2276.
- [11] A.C. Dürr, F. Schreiber, K.A. Ritley, V. Kruppa, J. Krug, H. Dosch, B. Struth, Phys. Rev. Lett. 90 (2003) 016104.