Growth mechanism of solution-deposited layers of the charge-transfer salt CuDDQ

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Charge-transfer (CT) salts such as copper-2,3-dichloro-5,6-dicyano-*p*-benzoquinone (CuDDQ) are promising components of reversible resistive memory switching devices. In the study presented here, we report on the composition of CuDDQ layers grown from acetonitrile containing solution onto copper-coated silicon substrates. According to Rutherford Backscattering Spectrometry (RBS) experiments, the CuDDQ film is homogeneously composed of copper and DDQ across its whole thickness, and the ratio between copper and DDQ is 1:1. A complex between copper and acetonitrile has been identified by Electro Spray Ionization (ESI) time-of-flight mass spectrometry as the main source of copper ions for the CuDDQ layer formation. In contrast, if ethanol is used as solvent, no copper-ethanol complex can be discerned from the ESI mass spectrum. This finding underlines the vital role of acetonitrile as the main copper source for the complexation reaction with DDQ. The continuous availability of the copper-acetonitrile complex in solution during the growth of the CuDDQ layers explains their homogeneity as determined by RBS.

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1 Introduction

Reversible resistive memory switching phenomena have been observed in various organic [1–3] as well as inorganic [4] material systems. Resistive switching refers to the observation that the system's electrical resistance can be intentionally and reversibly changed by the application of a voltage ramp [1, 2] (Fig. 1) or an electromagnetic field [5]. Memory-type switching specifies, that the resistance is stable in its respective state even when no external voltage is supplied to support the memory state. Resistive switching phenomena are interesting from a fundamental point of view such as to understand the underlying mechanisms of the switching. Moreover, from an applied perspective devices built from these systems could be used for the realization of computer memories [6].

Resistive switching phenomena in organic compounds have been investigated in material systems in which just one type of molecule is employed (e.g. DDQ) [3], as well as in systems in which the layer is composed of a complex between a molecule and a metal [1, 2]. In charge-transfer (CT) salts composed of a metal and an organic compound, these phenomena were firstly described by Potember et al. [2]. In their pioneering work, they found that the CT salt between copper and 7,7,8,8-tetracyanoquinodimethane (TCNQ), CuTCNQ, can be reversibly switched between two resistive states by the application of a voltage pulse. The resistive state remains stable even if no voltage is supplied to the system.

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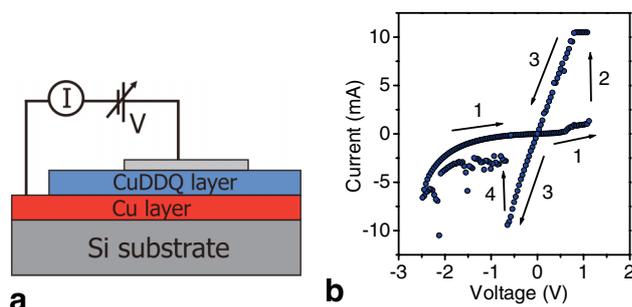
Fig. 1 (online colour at: www.pss-b.com)   (a) Schematic of the sandwich device used for electrical test-
ing. On top of the CuDDQ layer (which is usually about 100 nm thick) a metallic electrode (shown in
light grey) is deposited by vapour-deposition. (b) Resistive switching of a CuDDQ cell with a titanium top
contact. As the voltage across the molecular layer is swept as indicated by the arrows and numbers the
resistance of the layer changes spontaneously (numbers 2 and 4) from a high resistive state (1) to a low
resistive state (3).

Recently, it was found that CT salts based on copper and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone
(DDQ), CuDDQ, show resistive memory switching phenomena [1]. Sandwich cells could be reversibly
transformed between a high- and a low resistive state by the application of a voltage ramp or a voltage
pulse. A schematic as well as the switching of such a CuDDQ sandwich cell is shown in Fig. 1.

One intriguing property of these metal-organic CT salts is, that the preparation of layers and sandwich
cells for electrical measurements (Fig. 1a) is very straightforward: CuDDQ, for example, readily deposits
onto a metal substrate (for example a copper coated silicon wafer) that is dipped into a DDQ and aceto-
nitrile containing solution via a spontaneous redox reaction. Layers of CuDDQ as thick as 100 nm are
thus obtained within minutes. The copper ions that are incorporated into the CuDDQ film are supplied
from the copper substrate.

It has been reported by several authors [1, 2, 7] that acetonitrile is essential for the growth of metal
organic CT salts from solution, although the underlying mechanism has not been clarified. In order to
elucidate the switching mechanism and to optimize the growth process, it would be advantageous to
understand in greater detail the growth mechanism of the charge transfer salts, as well as the composition
of the deposited layers.

Here, we present details on the morphology of a CuDDQ layer investigated by atomic force micro-
scopy (AFM), as well as the composition of a CuDDQ layer as determined by Rutherford Backscattering
Spectrometry (RBS). Furthermore, the role of acetonitrile in the growth process has been identified by
Electro Spray Ionization (ESI) time-of-flight mass spectrometry.

2   Experimental

For CuDDQ film formation, the substrate (a degenerately doped silicon wafer covered with a 300 nm
thick layer of thermally grown SiO_2 and a 20 nm thick layer of copper deposited by thermal evaporation)
was first cleaned with 2 molar citric acid solution in order to remove the native copper oxide layer. After
rinsing with deionised water, acetone and isopropanol, the substrate was blow-dried with nitrogen. Sub-
sequently, it was immersed in a solution of 10% acetonitrile, 90% toluene with 0.75% DDQ for one
minute. Rutherford Backscattering Spectrometry (RBS) measurements were performed using He^+ ions of
a kinetic energy of 2 MeV with the incident beam normal to the substrate surface. He^+ ions that were
backscattered under an angle of 170° relative to the incident beam were detected. From the relative
intensities of the energy of the backscattered ions, the layer composition was determined using the soft-
ware package RUMP [8]. Electro Spray Ionization (ESI) time-of-flight mass spectrometry measurements
were performed on a home-built mass-spectrometer [9].
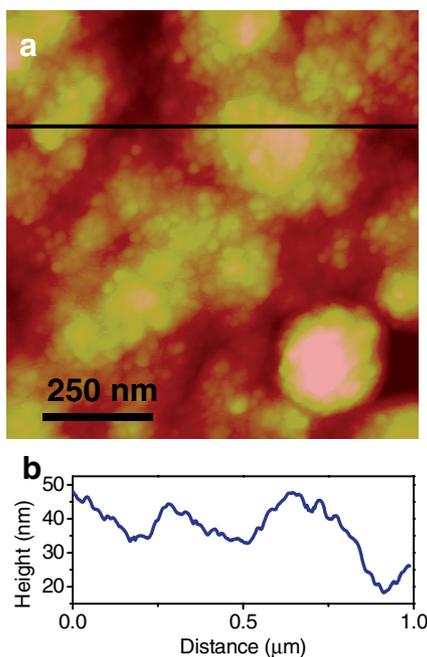
Fig. 2 (online colour at: www.pss-b.com) (a) Atomic Force Microscopy (AFM) image of a CuDDQ layer grown from solution. (b) Line scan at the position indicated by the black line in (a).

3   Results and discussion

CuDDQ layers grown from solution on a copper covered silicon substrate were investigated by Atomic Force Microscopy (AFM). A typical image is shown in Fig. 2. The layer has a root-mean-squared (RMS) roughness of about 10 nm, which is remarkably small considering the simple fabrication technique by which the layers were prepared. Compared to CuTCNQ layers prepared by the same method, the CuDDQ layers are comparably smooth [10].

In order to gain further insight into the composition of the CuDDQ films, Rutherford Backscattering Spectrometry (RBS) measurements were performed. RBS is a versatile technique to investigate the depth distribution of the elements in layered structures. In the RBS data shown in Fig. 3 the histogram over the kinetic energy of the He$^+$ ions backscattered from the CuDDQ film is displayed. The layer composition has been determined by simulating this spectrum with the software package RUMP [8]. Figure 3 shows the fitted RBS spectrum along with the measured data. The layer thicknesses that gave the best agreement to the experimental data are shown in the inset of Fig. 3. In this simulation, the ratio between copper and DDQ was chosen to be 1:1. Simulations with different ratios between copper and DDQ yielded less satisfactory results. Copper and DDQ were assumed to be evenly distributed in the layer for the simulation. A homogeneous distribution of copper and DDQ across the whole thickness of the film has been found for CuDDQ layers as thick as 130 nm.

In order to determine the role of acetonitrile in the growth process of CuDDQ on the copper surface, ESI mass spectrometry measurements were performed. It is well documented, that acetonitrile is needed for the solution-based formation of CT salts such as CuTCNQ and CuDDQ [1, 2]. However, the role of acetonitrile in the formation of for example CuTCNQ has not been clearly identified [7]. For our study, we immersed a cleaned copper rod in an acetonitrile solution, and investigated the solution by ESI mass spectrometry. A complex between copper and acetonitrile (MeCN) could be detected in the ESI spectrum (Fig. 4). This finding indicates that copper ions can be readily dissolved by complexation with acetonitrile. The CuDDQ complex is then formed via ligand exchange, wherein DDQ replaces the MeCN. In contrast, if a cleaned copper rod is immersed in an ethanol solution of DDQ, no complex between copper and ethanol can be discerned in the ESI mass spectrum.
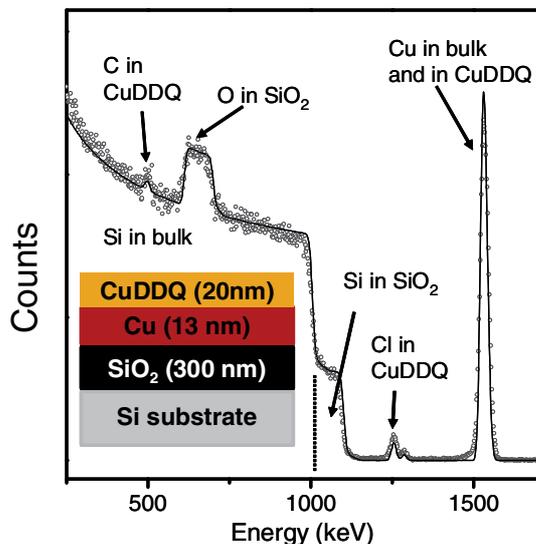
Fig. 3 (online colour at: www.pss-b.com) Rutherford Backscattering Spectrometry (RBS) data of a CuDDQ film. The solid line is a simulation with the RUMP software package. The layer thicknesses were chosen so that the simulation fits best to the measured data (open circles). The inset shows the thicknesses of the layers used for the simulation.

The different behaviour of acetonitrile and ethanol becomes even more apparent, when DDQ is added to a copper rod immersed in one of these solvents. The acetonitrile solution that a copper rod has been immersed into turns red right away, whereas the ethanol solution under the same conditions turns yellow. While pristine DDQ is yellow, the red colour has been attributed to the CuDDQ complex in solution [1]. The above observations underline the vital role of acetonitrile acting as a complexing agent that makes copper ions available for reaction with DDQ.

If our interpretation that the complexed copper ions are the main source of copper for the CuDDQ film growth is correct, the homogeneity of the CuDDQ layers as determined by the RBS measurements is understandable: Since copper ions as well as DDQ both are solvated and available for the growth of CuDDQ layers, the solution concentration of both species will not depend on the thickness of the CuDDQ layer. This explains the homogeneous distribution of copper and DDQ throughout the CuDDQ layer as measured by RBS. In contrast, if the main source of copper ions for film growth were ions directly from the copper film (both, the solvated copper ions as well as copper directly from the bulk had been suggested as copper source for the film growth from solution for films of CuTCNQ) [7], a non-homogeneous distribution of copper within the CuDDQ film could be expected at least in thick films, since copper ions would have to diffuse through the already grown CuDDQ film in order to take part in the growth process.
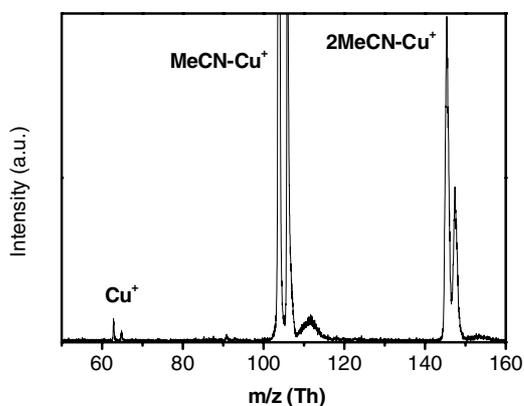
Fig. 4 Electro Spray Ionization (ESI) mass spectrum of copper in acetonitrile (MeCN). For the preparation of the solution a copper rod was immersed into an acetonitrile solution. Prior to immersion, the copper rod was cleaned with 2 molar citric acid to remove any copper oxide on the surface.

4 Conclusion

In summary, we have demonstrated that CuDDQ layers grow from DDQ and acetonitrile containing solution onto a copper coated silicon substrate. The RMS roughness of CuDDQ layers obtained in this manner was determined by AFM measurements to be 10 nm. It is hence concluded that this solution deposition method, despite its simplicity, constitutes an effective approach to the fabrication of thin films of CuDDQ. As deduced from ESI mass spectrometry and RBS, a complex between acetonitrile and copper ions is formed which acts as a continuous source of copper ions, thereby enabling the growth of homogenous CuDDQ layers with a copper:DDQ ratio of 1:1.

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