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Self-Aligned Growth of Organometallic Layers for Non-Volatile Memories: Comparison of Liquid Phase and Vapor Phase Deposition

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Abstract

Deposition methods for the self-aligned growth of organometallic charge transfer complexes for use as a conductivity modulated, non-volatile switching layer are presented. First, a deposition from liquid phase is investigated and a model for film growth is derived. Then, a novel deposition technique for charge transfer complexes, namely selective organic vapor-phase deposition, is introduced which excels in selectivity and homogeneity. In particular, silicon dioxide layers exposed to the precursor molecules during processing remain completely uncovered, whereas copper pads in contact holes are rapidly filled with the desired layer of the charge transfer complex. Then, both deposition methods are compared regarding reproducibility, selectivity, homogeneity, and the ability to selectively grow thin films in small structures with diameters below 200 nm. Finally, electrical switching properties are investigated and the switching mechanism for the present charge transfer complex is discussed.

Keywords: non-volatile memory; organometallic layer; vapor phase deposition

Introduction

As prospective successors for Flash or DRAM memory, several new concepts for data storage have been intensively studied in recent years. Conductivity modulated memory designs experienced a major focus of investigation. Conductivity modulated memory technologies include magnetoresistive random access memory [1, 2], programmable metallization cell memory or conductive bridging RAM [3, 4], and chalcogenide-based phase-change memory, [5] as well as organic memory concepts [6, 7], which employ a layer of organic or or-

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ganometallic material to achieve reversible, non-volatile conductivity switching.

One of the most promising organic memory technologies incorporates the charge transfer complex copper-tetracyanoquinodimethane (CuTCNQ) as the active layer and was first described by Potember et al. [8-10]. Charge transfer (CT) complexes consist of an electron donor and an electron acceptor. In the case of CuTCNQ, the TCNQ molecule acts as the electron acceptor while each copper atom is acting as an electron donor. However, a number of other metals and several electron-rich organic molecules have been investigated as feasible electron donors [11, 12].

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A characteristic property of a CT complex is the quantity of electron transfer, i.e. the extent to which donor electrons are transferred towards the electron acceptor. Due to a typically limited electron transfer, the bonds of a CT complex are weaker than covalent and even hydrogen bonds, but they are usually strong enough to build crystalline structures [13].Resistance switching in thin films of CT complexes has been obtained by voltage pulses of different amplitudes and polarity, and switching times below 25ns have been achieved [8]. Although the theory of operation for this kind of organometallic memory is not yet fully understood, it is assumed that the amount of electron transfer between the acceptor and donor, which determines the conductivity of a CT complex, can be permanently modulated under an electric field [14, 15]. The conductivity of a CT complex is initially low because the donor electrons have been (partially) transferred to the acceptor, resulting in positively charged metal ions unable to sup-port current conduction ("off-state"). The charge transfer can be reverted applying an electrical pulse, leading to the separation of donor electrons from the acceptor molecule, finally resulting in neutral copper atoms. These atoms are capable of driving large currents due to pairs of free (non-bonded) valence electrons, resulting in a high conductivity of the CT complex layer - the so called "onstate". This model has been supported by Raman spectroscopy which has proven a relation between the conductivity of the material and the content of neutral copper [16, 17].

The deposition of layers of organometallic CT complexes has been achieved by several ways. Basically it requires that the metal and the organic acceptor are brought into contact to each other at the substrate. Then, a chemical reaction of the metal and the organic component can be observed either at elevated temperatures or, when using a catalyst, even at room temperature.

Providing the metal component as a thin film on a substrate and supplying the organic acceptor in a second step offers important advantages for the fabrication of a memory layer. Firstly, the deposition is highly selective on exposed metal layers and will not commence on other materials. Therefore, a selective deposition of the memory layer can be achieved by masking the metal layer with silicon dioxide for instance. Furthermore, the seed metal can also be used as one electrode of a CT complex memory cell. Consequently, the memory cells can be fabricated in contact holes of the metallization layer in the back-end-of-the-line of a CMOS process, allowing for easy processing of multilayer memory stacks for use in a matrix configuration [6].

In this work, an alternative charge transfer complex (CT) between copper, acting as the electron donor, and a selected electron accepting organic component is investigated, which showed promising electrical properties for

use as a memory layer in a previous, internal study. The organic component is a quinone derivative with heavily electron drawing substituents. The organometallic thin film can be fabricated by several means. A commonly used technique is liquid phase deposition. Experiments employing a variation of process time as well as catalyst concentration lead to a model describing the reaction dynamics. A novel deposition method which was adopted from chemical vapor phase deposition (CVD) processes is also introduced. The comparison between these two deposition techniques as well as results of the electrical characterization of fabricated memory cells concludes this work.

Deposition Methods and Sample Preparation

a) Sample Preparation

Basic investigations were carried out on samples consisting of oxidized silicon substrates, which had a metal stack of 50 nm titanium tungsten followed by 500 nm copper evaporated on top. In order to examine the selectivity of the deposition processes, additional samples from a copper chemical mechanical polishing process were used. These samples had 200 nm thick layers of silicon dioxide and nitride deposited on top of structured copper lines. Finally, contact holes of diameters from 5 μ m down to 200 nm were opened into the oxide/nitride by means of lithography and subsequent etching, exposing copper pads of 250 nm thickness.

Prior to deposition of the organometallic layers, all samples were treated in 2-molar citric acid to remove any native copper oxide, which would otherwise hinder or prevent the deposition process. Then, the CT complex was deposited from liquid or vapor phase. The thickness of deposited layers was measured from cross-sectional scanning electron microscopy (SEM) images. Finally, a metal electrode of titanium or aluminum was evaporated on top of the organometallic layer for some of the samples.

b) Liquid Phase Deposition

For the liquid phase deposition, the organic component, which is solid at room temperature, was solved in toluene. To initiate the reaction, either the temperature must be sufficiently high (above approx. 120 °C) or a catalyst must be used. For this work, a liquid phase dipcoating process known from CuTCNQ deposition was initially used, where acetonitrile acts as the catalyst [8]. A substrate with exposed copper pads was then brought into contact with the solution and the copper-based organometallic charge transfer complex formed on the cop-per electrodes.

Immersion time ranged from 15 s to 8 min and the acetonitrile concentration in the solution was varied from 2.5% to 10%.

c) Vapor Phase Deposition

Deposition from vapor phase requires the organic component to be evaporated. The organic vapor is then directed into a furnace where it reacts with exposed copper surfaces of the heated substrates.

Initially, this method was tested using a simple deposition setup, where the substrates and the organic component were placed besides each other at atmospheric pressure in a stainless steel cylinder, which was heated to temperatures between 150 °C and 190 °C using an oil bath.

To enhance the homogeneity and reproducibility of this process, a more versatile deposition system was developed. A solution of the organic component was injected into an evaporator and transported to a temperature controlled furnace by a carrier gas flow (argon) which is precisely controlled by a mass flow controller. A vacuum pump ensures a steady gas flow and a constant pressure during processing and removes excessive acceptor molecules and reaction byproducts from the system. This process setup enables the independent variation of several deposition parameters (e.g. evaporation and deposition temperatures, gas flow, pressure, precursor concentration) that can be easily adjusted in order to optimize the chemical, physical, and electrical properties of the deposited films.

Results and Discussion

a) Liquid Phase Deposition

In order to determine the deposition dynamics inherent to the liquid process, the influence of different process parameters on the grown CT complex films has been investigated. Fig. 1 shows the dependence of process duration and catalyst concentration on the film thickness.



Fig. 1: Growth rate of the CT complex at different acetonitrile concentrations (marks), fitted by derived model (lines)

For each acetonitrile concentration used, the resulting film thickness was proportional to the square root of the immersion time. A similar dependence is known from diffusion limited processes like the oxidation of silicon, which was modeled e.g. by Deal and Grove [18]. There, oxygen or water molecules diffuse through an existing silicon dioxide layer to the silicon substrate, where the oxygen atoms react with the silicon resulting in the growth of silicon dioxide. With increasing oxide thickness the gradient of the oxygen concentration across the oxide decreases. Hence, the flux of oxygen atoms through the oxide is reduced and the growth rate decreases.

A similar approach was used to establish a model describing the liquid phase deposition of copper-based organometallic charge transfer complexes: Given that the copper atoms are distinctly smaller than the organic molecules, the diffusion constant for the metal atoms should be significantly higher. However, without catalyst no growth of the CT complex layer was observed at room temperature. This is probably due to the high activation energy required to remove copper from the substrate. This energy can be reduced by adding acetonitrile to the solution. Thermodesorption experiments revealed that molecules of acetonitrile are incorporated into the CT layer during film growth. The concentration of acetonitrile at the metal/CT layer interface is assumed to be proportional to the acetonitrile concentration of the solution. A close investigation of Fig. 1 reveals that the deposition rate increases by a factor of 4 when the acetonitrile concentration doubles. In contrast, no measurable impact on the deposition rate was found for a wide range of concentrations of the organic component (between 0,375% and 3%), and, therefore, the organic component can be excluded as the limiting factor for deposition.

From these observations, the following model for the deposition of a CT layer on a metal (e.g. copper) substrate is proposed:

- 1. When the organic solution is brought in direct contact with the metal substrate, a thin CT layer is formed. The deposition rate is initially limited by the reaction constant to form the CT complex. Initially, the reac-tion rate is high compared to the diffusion rate. However, once a thin layer of the CT complex has formed, the amount of metal atoms available for reaction at the surface becomes low, as more or less all metal atoms are bonded.
- Catalyst molecules that are incorporated into the CT layer will release new metal atoms at the metal/CT complex interface. This generation of metal atoms and their diffusion were not observed without catalyst.

- 3. As the number of non-bonded metal atoms at the CT layer surface decreases, a concentration gradient of non-bonded metal atoms over the CT layer ensures a steady supply of metal atoms. The number of activated metal atoms heavily depends on the acetonitrile concentration at the metal/CT complex interface.
- Finally the reaction of metal atoms at the CT layer/solution interface with molecules of the organic electron acceptor from the solution takes place increasing the CT layer thickness.

The growth-limiting reaction kinetics can be derived by discussing the reaction kinetics from those 4 steps sequentially. Step 1 is a reaction limited process of very short duration and will be neglected. Step 2 and 3 describe the activation of metal atoms and the subsequent diffusion through the existing layer of the CT complex. Finally, step 4 is governed by another reaction limited process which can be neglected in comparison to the long diffusion times of steps 2 and 3.

Therefore, the deposition of an organometallic CT layer from liquid phase at room temperature is a diffusion limited process. Using a mathematical approach similar to the description of silicon oxidation by Deal and Grove [18], requiring that the flux of metal atoms through the interfaces and the bulk is steady, we find that the density of diffusing metal atoms J_m due to a gradient in the concentration of activated metal atoms from the metal/CT layer interface $C_{m,i}$ to the CT layer surface $C_{m,s}$ is given by Fick's first law of diffusion:

$$J_{m} = D_{m} \frac{C_{m,i} - C_{m,s}}{x_{om}} , \qquad (1)$$

where x_{om} is the thickness of the organometallic layer and Dm the diffusion constant of the metal atoms in the CT layer. Due to the rapid reaction of non-bonded metal atoms at the interface, $C_{m,s}$ is very small and can be neglected. Assuming that 2 molecules of acetonitrile are required to release a metal atom from the lattice into the CT layer, the law of mass action predicts that

$$C_{m,i} = k_r \cdot C_{acn}^2 , \qquad (2)$$

when the metal concentration in the metal layer is constant. Here, C_{acn} describes the acetonitrile concentration at the metal/CT layer interface which is by assumption proportional to the acetonitrile concentration in the solution, and k_r is the proportionality factor describing the rate constant for catalytic generation of free metal atoms.

The growth rate for a CT layer of thickness x is only proportional to the flux of released metal atoms J_m and the number of metal atoms per area N_m that are incorpo-

rated into the layer. Using Eq. (1) and (2), the growth rate is given by

$$\frac{dx_{om}}{dt} = \frac{J_m}{N_m} = \frac{D_m}{N_m} \frac{k_r \cdot C_{acn}^2}{x_{om}} .$$
(3)

Integrating Eq. (3), the dependence of the thickness d on the process duration t can be calculated as

$$d = \sqrt{\frac{k_r \cdot D_m}{N_m} \cdot C_{acn}^2 \cdot t} \quad . \tag{4}$$

With this dependence, the deposition rate of organometallic layers grown by the liquid phase deposition at room temperature can be predicted as shown in Fig. 1 (analytical model (3) with k_r as a single fit parameter).

In our experiments, depositions were successfully achieved in contact holes with diameters down to 200 nm. Using a substrate with contact holes of 500 nm diameter, the selectivity of the deposition process from a solution with acetonitrile being the catalyst was investigated. From a typical cross-sectional SEM as image presented in Fig. 2, the selectivity of the CT layer deposition on the copper layer compared to a SiO2 surface is approximately determined to be 3:1 for the given solution, i.e. significant deposition of the CT layer on the silicon dioxide occurred.



Fig. 2: SEM images of CT layers grown after 4 minutes from a solution of the organic component in toluene with 5% acetonitrile in a contact hole of 500 nm diameter

The following explanation accounting for this lack of selectivity is considered: During film growth, a fraction of the CT complex layer is solved in acetonitrile (going along with a characteristic color change of the solution). These free complex ions are re-adsorbed at the surface of the silicon dioxide layer in proximity to the contact holes. For a solution with 5% acetonitrile, a thin layer of the CT complex could be observed in the vicinity of contact holes up to a distance of 10 μ m.

Using propionitrile as catalyst, the selectivity of the deposition was enhanced, because the solubility of the CT complex in the catalyst is reduced by the additional methyl-chain of the propionitrile molecule. However, the

effectiveness of the catalyst is also reduced, resulting in a significantly slower deposition rate.

Also, it is evident from Fig. 2 that the deposition rate for these samples is significantly lower than for the unpatterned copper samples used to derive the results shown in Fig. 1.

b) Vapor Phase Deposition

In an alternative approach we have investigated a deposition technique adopted from chemical vapor phase deposition. Initially, a simple process setup using a stainless steel container heated oil bath was used as described above. After exposing the sample to the vapor of the organic component for 15 minutes, thin films of approximately 300 nm thickness and with low surface roughness were achieved. The SEM image of a CT layer grown by vapor phase deposition for 120 minutes at 175 °C is given in Fig. 3, where a 1.2 μ m thick film of a homogeneously grown CT complex on a copper layer of 500 nm thickness is shown.



Fig. 3: Cross-sectional SEM image of a homogeneous thin film of the CT complex on a 500 nm thick copper substrate. The CT complex was deposited by a CVD process in 120 minutes at 175 °C

Fig. 4 shows the SEM image of contact holes (500 nm diameter) filled with 120 nm thin layers of the CT complex, demonstrating the local deposition properties of this technique.



Fig. 4: SEM cross-sectional image of contact holes after CVD deposition of the CT complex for 8 minutes at 175 °C

Since sample preparation for SEM imaging requires the samples to be broken, the ductile copper layer is partially pulled out from under the pad. Additionally, no CT layer is formed on the silicon dioxide, making this a highly selective deposition method. However, good thickness homogeneity across the sample could not be achieved due to the process setup. The evaporation of the organic component takes place asymmetrically on one side of the samples resulting in a steep concentration gradient of the vaporized component across the sample. A strong dependence of the distance from the evaporation source on the thickness was observed. This dependence indicates that in contrast to the liquid phase deposition at room temperature, the vapor phase deposition process at low pressure is no longer limited by the diffusion of metal atoms through the CT layer. We believe that in the present case this is due to enhanced copper diffusion at elevated temperatures. Under these conditions, the deposition rate is governed by the transport of the evaporated organic component to the CT layer surface, where it is adsorbed and the reaction with neutral copper atoms commences. The CT complex formed by this process is stable at the elevated process temperature, while excessive acceptor molecules and reaction byproducts as well as contaminants are volatile and can be pumped out of the system.

c) Comparison of Deposition Methods

Analysis of SEM images, e.g. Fig. 3, indicates that layers of the charge transfer complex deposited with both techniques are amorphous. This provides an advantage over layers of CuTCNQ, where homogeneity was identified as a main problem due to polycrystalline thin film growth, along with the existence of two different crystal-line phases [16].

Both deposition methods allow for reproducible layer fabrication, although the vapor phase deposition can be fine tuned more precisely. Surface roughness appears to be no issue for both deposition methods and contact holes of diameters below 200nm were uniformly filled with the CT complex.

Excellent selectivity of the deposition on the metal layer can be easily performed by vapor phase deposition, allowing for self-aligned growth of the active layer in memory cells. In order to achieve comparable results regarding the deposition of the selected charge transfer complex from liquid phase, additional research is required.

Due to the diffusion limited nature of the liquid phase deposition process, the process window to achieve a desired target thickness can be adjusted by the catalyst concentration (compare growth rates from Fig. 1). Unfortunately, a negative effect of catalyst molecules that are incorporated into the CT layer during deposition on the electrical properties cannot be ruled out. The vapor phase deposition offers an even wider number of process parameters that can be altered towards the desired deposition rate, at the same time reducing contamination due to the high temperature (up to 210°C) and low pressure (1mbar).

Finally, the variety of process parameters of the vapor phase deposition process allows the alteration of layer properties while still offering enough additional parameters for excellent controllability of the deposition rate. The advantages and draw-backs of both deposition techniques are summarized in Table 1.

Table 1: Comparison of liquid and vapor phase deposition methods under investigation

	Liquid phase	Vapor phase	
Homogeneity	Good	Good	
Reproducibility	Good	Very good	
Surface Roughness	<10 nm	<10 nm	
Selectivity on Metal	33%(*)	100%	
Filling of Contact Holes	< 200 nm	< 200 nm	
Contamination during Deposition	High	Low	
Complexity of Process Parameters	Low	Very High	
Controllability of Layer Properties	Limited	Excellent	
(*) use of different catalyst possible, additional research required			

d) Investigation of Layer Composition

Layers deposited from vapor phase at different temperatures were analyzed in respect to their copper content by x-ray photoelectron spectroscopy (XPS) and compared to samples prepared by liquid phase deposition. The results for these samples, which were sputter cleaned for 1 minute prior to XPS measurements, are listed in Table 2.

 Table 2:
 Copper content of CT layers deposited at different temperatures, determined by XPS

Process	Temperature	Copper cont.	Carbon cont.
Vapor	215°C	37,4%	30,9%
Vapor	180°C	14,4%	60,9%
Liquid	20°C	8,7%	67,3%

The strongly increased copper content in the CT layers deposited at higher temperatures can be explained by thermally enhanced copper activation and diffusion.

Chemical analyses were conducted to verify that both deposition methods yield similar layer compositions. The results of Fourier transform infrared spectroscopy (FTIR) measurements of sample layers fabricated by both techniques are given in Fig. 5. The FTIR spectra indicate that the bond properties in the CT complexes are in good agreement for layers fabricated with both deposition methods.



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- Fig. 5: FTIR reflectance spectra of CT layers, deposited by deposition from liquid phase at room temperature (dashed line) and vapor phase deposition (solid line) at 175 °C
- e) Electrical Characterization

To confirm that layers of the deposited CT complex exhibit switching behavior, electrical measurements were conducted on samples with evaporated aluminum and sputtered titanium electrodes. Fig. 6 shows one of the I(V)-curves obtained from these measurements.

The memory cells show resistive switching at about ± 1.5 V. However, the transition from low to high resistance state is performed gradually with increasing voltage. Electrical measurements also indicated that the conductivity in the "off"-state increases with increasing copper content, which is reasonable as more neutral copper atoms which are not bonded at all are present in the CT layer, each capable of providing its valence electrons to conduction. Therefore, the vapor phase deposition is suited to set the low conducting resistance state to a desired value by choice of deposition temperature.



Fig. 6: I(V)-curve of memory cell with 200 nm thin CT layer fabricated using liquid phase dip-coating process, top electrode: titanium

Conclusion

Two deposition methods for the self-aligned growth of organometallic charge transfer layers for use in nonvolatile memory cells were compared.

For liquid phase deposition, a model describing the reaction kinetics was deduced which allows for the prediction of deposition rates. Selectivity issues were addressed by altering the composition of the solution, i.e. by exchanging the catalyst.

A novel vapor phase deposition technique for CT complexes, capable of selectively filling contact holes with diameters below 200 nm, is introduced. This method excels over the liquid phase deposition with respect to selectivity and versatility, offering a wider range of process parameters that are independently controllable. Additionally, we demonstrated that alteration of the process temperature directly affects electrical properties of the CT layer.

Obviously, the equipment required for the deposition of CT complex layers from vapor phase is more expensive than for layer fabrication by a liquid phase process. However, once established, the vapor phase deposition is free of contaminants and requires no additional processing steps (e.g. rinsing, drying), that are unavoidable when applying wet chemistry. Additionally, less expensive chemicals are required besides the organic component, resulting in lower production costs for high volume applications. Also considering the knowledge readily available from standard CVD processes, vapor phase deposition is expected to be superior for industrial production.

Both processes are compatible with existing CMOS technology manufacturing equipment. On one hand, liquid phase deposition can be easily transferred to a spincoating system commonly used in lithography for instance. Furnaces and evaporation systems, on the other hand, are routinely used and a wide range of systems is readily available, keeping time-to-market costs low for this deposition technique while offering excellent controllability of deposition parameters.

The chemical structure of CT layers fabricated with both deposition methods is similar, leading to the assumption that memory layers deposited with these techniques show comparable electrical behavior.

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