Angewandte Chemie

Organic Electronics

DOI: 10.1002/anie.200805329

Room-Temperature Growth of Silicon Oxide Nanofilms: New Opportunities for Plastic Electronics

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atomic layer deposition · Langmuir–Blodgett films · nanostructures · organic transistors · silicon oxide

MOSFETs (metal oxide semiconductor field effect transistors, Figure 1) are the most ubiquitous electronic circuit elements, and are present today in almost every electrical device. The basic functions and the materials that MOSFETs are made of have essentially remained unchanged in the more than 40 years that they have been in production. In contrast, the size of MOSFETs, as measured by the so-called gate length L (Figure 1), has shrunk from over 20 μm in the first marketed MOSFETs to 20 nm in the current chip generation. The smallest feature of these nanosized transistors is the so-called gate oxide, which is the thin silicon oxide layer that separates the gate electrode from the bulk silicon. The thinner the gate oxide, the lower the required operating voltage for a certain drive performance and the lower the power consumption and power dissipation, which are the main limiting factors in today's ultralarge-scale integrated circuits.[2]

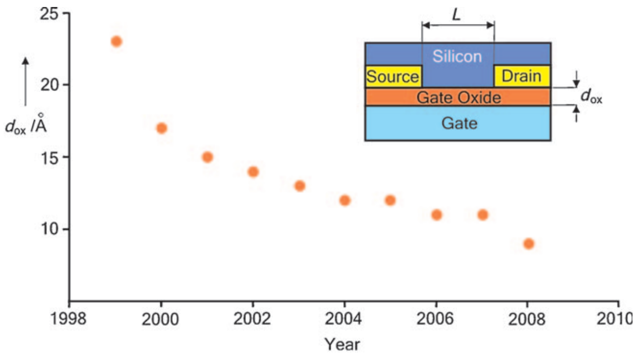

Figure 1. Reduction of the gate oxide thickness d_{ox} in commercial MOSFETs over the last decade. Data from Reference [1].

Concomitant to the overall size of MOSFET transistors, the thickness of the gate oxide has decreased from about one micrometer in the first generation MOSFETs to one nanometer in the latest generation of chips, and is predicted to further shrink to sub-nanometer dimensions. In this thickness range, the oxide layer is only a few silicon atoms thick and can no longer be considered a macroscopic, homogenous phase, since interfacial effects arising from surface defects, contaminations, and surface roughness start to dominate the layer properties.[3] Accordingly, the conventional technique for oxide growth, namely thermal oxidation with O_2 at 750–1100 °C, which has been used successfully over the past 40 years, is reaching its limits when it comes to the growth of sub-nanometer-thick oxide films, and much effort has lately been put into the development of alternative growth methods that offer precise control over the layer thickness and homogeneity at the molecular scale.[4]

A second, equally demanding, challenge is the development of methods for the growth of the gate oxide in a new generation of transistors based on organic semiconductors (organic field effect transistors, OFETs). OFETs can be used in low-cost, printable integrated circuits on large-area, flexible substrates (plastic electronics), and hold great promise for applications such as electronic price labels, flexible displays, and radio frequency identification tags.[5] OFETs have the same basic structure and operation modes as the inorganic MOSFETs, but are made, at least partly, of organic materials and therefore require low-temperature, solution-based fabrication methods.

One of the most promising methods for the growth of a thin film that combines precise control over the thickness with low-temperature, solution-phase protocols is based on the concept of atomic layer deposition (ALD), which was developed more than 20 years ago for the growth of thin ZnS films for electroluminescent displays.[6] ALD is a discontinuous, sequential growth method,[4e] where a film of certain composition S is grown one monolayer at a time by splitting a suitable film-formation reaction involving two precursors A and B ($A + B \rightarrow S$) into two half-reactions, which are performed sequentially and repeatedly on the substrate surface: In step A, a monolayer of reactant A is adsorbed on the surface. In step B, a monolayer of reactant B is adsorbed on top of A, where it reacts quantitatively with A to yield one monolayer of the desired film composition S. The whole process is then repeated to deposit a second, third, and forth monolayer, and so on. Provided that the adsorption of precursor A and B is complete and self-limiting at the monolayer level (which means that exactly one monolayer is formed) and that the reaction $A + B \rightarrow S$ proceeds fast and quantitatively on the surface, exactly one monolayer of S is produced in each A/B reaction cycle and the overall film

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thickness can be controlled “digitally” by the number of applied A/B cycles.

The growth of silicon oxide and other metal oxide films by ALD was pioneered by George and co-workers,[7] who used the gas-phase deposition of one monolayer of $SiCl_4$ on silicon substrates followed by one monolayer of H_2O to grow SiO_2 films layer by layer according to the overall reaction $SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl$. By using pyridine as a catalyst, they could achieve a linear rate of film growth of 1.35 Å per cycle at room temperature over 250 cycles to achieve a total thickness of 35 nm. A practical application of this process is hampered, however, by the complex involvement of pyridine in the growth reactions.[7c] In a related process, Yamaguchi et al.[4d] used tetraisocyanatesilane $Si(NCO)_4$ and triethylamine to deposit SiO_2 at 150 °C with a growth rate of 1.2 Å per deposition cycle. They achieved very smooth and homogeneous films; however, the growth rate of 1.2 Å corresponds to only about 50 % of a full SiO_2 monolayer and indicates a less densely packed oxide structure.

In a recent publication by Kim et al.,[8] the concept of the growth of ultrathin silicon oxide layers by ALD was revived in a modified form. The authors used an organic polymer containing polyoctahedral silsesquioxane substituents as the silicon source, which was deposited in a layer-by-layer mode onto a quartz substrate (step A) by using the Langmuir–Blodgett (LB) technique and then subsequently oxidized by short-wavlength UV irradiation (step B) to SiO_2 and volatile hydrocarbon oxidation products. The film thickness was found to decrease upon oxidation to one fifth of the thickness of the precursor film before oxidation, which corresponds to a 0.4 nm thick SiO_2 layer for each precursor monolayer. In contrast to the classical ALD scheme of alternating between step A and step B (ABABABAB), a multilayer of desired (precursor) thickness was prepared by repeated LB deposition and was afterwards oxidized in one step to yield a pure SiO_2 layer (AAAAB). Analogous to classical ALD processes, the resulting oxide thickness was controlled by the number of deposited LB layers and showed a strictly linear growth rate of 0.4 nm per layer up to 200 monolayers, which corresponds to an oxide film thickness of 80 nm.

The composition and quality of the obtained oxide films were comprehensively characterized by a range of different techniques, including spectroscopic (FTIR, UV/Vis, XPS), imaging (AFM), and micromechanical methods (nanoindentation), and yielded the consistent result that these films grow perfectly uniformly and flat, and are essentially indistinguishable from thermally oxidized SiO_2. Most importantly, the SiO_2 films showed a uniform Si^{4+} concentration profile with no Si^{3+}, Si^{2+}, or Si^{+} suboxide species present, which are often unavoidable with other preparation methods (including thermal oxidation) and which degrade the electrical properties of the gate oxide layer.[3a,9] Finally, it was also shown that, because of the rapid oxidation and removal of the hydrocarbon portion in the polymer precursor films by UV light, these layers are ideally suited for photopatterning and the direct writing of SiO_2 patterns on the surface (Figure 2).

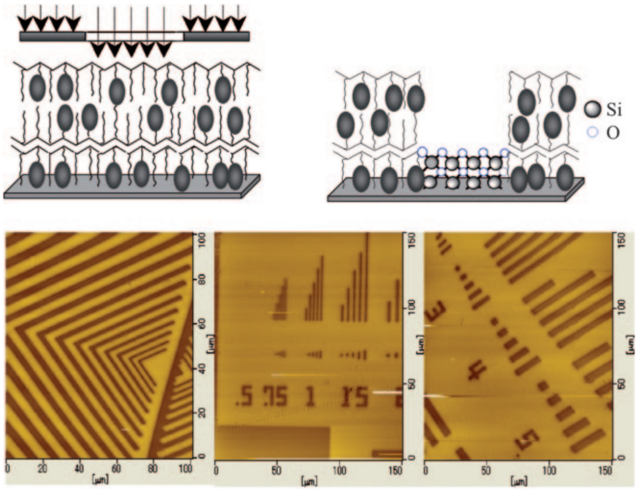

Figure 2. AFM images of photopatterned polymer/SiO_2 surfaces obtained by UV irradiation and oxidation of the hydrocarbon groups of the precursor polymer film. Reprinted with permission from Reference [8]. Copyright (2008) American Chemical Society.

In regard to practical applications of this new growth method for the high-throughput manufacture of OFETs, the drawbacks are the complex synthesis of the precursor and the slow and laborious LB deposition process. A viable alternative for the self-limiting adsorption of the precursor might be molecular self-assembly, which is a solution-based room-temperature process that results in high-quality monolayers from simple, commercially available hydrocarbon precursors on a wide range of different substrates, including organic polymers.[10] Vallant et al.[11] have reported on the growth of ultrathin SiO_2 films based on the self-assembly of organosilane monolayers on silicon, mica, and gold substrates. They used an ALD-type binary reaction sequence (Figure 3) consisting of the formation of a self-assembled alkylsiloxane monolayer $RSiO_x$ (step A), followed by oxidation and removal of the hydrocarbon groups by UV irradiation/ozone (step B), which resulted in a layer-by-layer deposition of silicon oxide with a strictly linear growth rate of 2.7 Å per cycle.

Another critical issue regarding the use of inorganic gate oxides in organic transistors is certain intrinsic limitations compared to organic dielectric materials.[12] In general, the dielectric layer has a much larger influence on the performance of OFETs than inorganic MOSFETs. Parameters such as interface roughness, surface composition, and defect density of the gate dielectric have been shown to critically affect the transport and the mobility of the organic semiconductor charge carriers.[5b,12b] Inorganic oxides, in particular, often act as electron traps through their surface hydroxide groups and essentially prevent any n-type behavior of organic semiconductors.[13a] Various surface treatments, such as coating with inert, hydrophobic layers, have been shown to partly remove these traps and enable n-FET conduction.[13] However, hydroxide-free, organic polymers are promising alternatives to SiO_2 as gate dielectrics in organic transistors which allow both p-type and n-type OFETs[12] and result in higher mobilities of the charge carriers and more reliable properties of the device compared to the highly variable performance of SiO_2-based OFETs. An inherent disadvantage of organic dielectrics, on the other

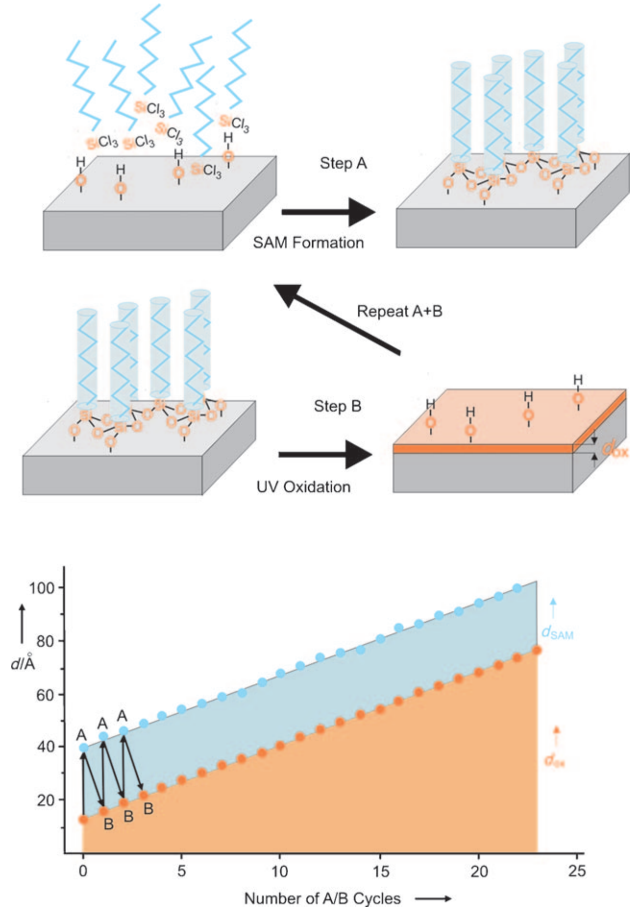

Figure 3. Layer-by-layer growth of silicon oxide films through repeated adsorption and oxidation of self-assembled organosilane monolayers. Data from Reference [11].

hand, are their relatively low dielectric constants ($k<10$) compared to the "high-k" inorganic oxides such as ZrO_2 ($k=22$), HfO_2 ($k=20$), and TiO_2 ($k=40$), which are currently being intensely investigated as inorganic substitutes for SiO_2.[12a] A further limitation is the fact that current techniques for the growth of polymer films can produce uniform, pinhole-free films barely thinner than 10–20 nm. Novel growth methods such as atom transfer radical polymerization (ATRP) can, in principle, produce significantly thinner organic dielectric films[12f] and could eventually catch up with the more advanced inorganic film growth techniques. At present, it is hard to predict whether the first commercial organic transistors will be all-organic or whether SiO_2 or some "high-k" inorganic oxide will prevail as the superior gate dielectric material.

[1] ITRS International Technology Roadmap for Semiconductors, www.itrs.net.

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