Observation of Precursor Control over Film Stoichiometry during the Chemical Vapor Deposition of Amorphous $Ti_xSi_{1-x}O_2$ Films

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As the thickness of the gate oxide in field effect transistors approaches 2 nm, direct tunneling will lead to unacceptable leakage currents, making it necessary to replace the silicon dioxide layer with a material possessing a higher dielectric constant. Potential replacements include TiO_2,[1−3] ZrO_2,[4−6] Ta_2O_5,[7,8] and various perovskites (e.g., $Ba_xSr_{1-x}TiO_3$).[9−11] An important consideration in integrating a new material is its microstructure. In particular, for the thin films necessary in microelectronics, surface roughness and grain boundaries resulting from polycrystalline films can have an undesirable effect on properties such as the dielectric breakdown and leakage current. To minimize roughness and grain boundaries, the high κ material can be made amorphous by combining it with a low κ, glass-forming oxide such as SiO_2. Titanium silicon oxide films have been produced by sol−gel,[12,13] flame hydrolysis,[14,15] and plasma-enhanced CVD[16,17] for optical applications and some reports of their electrical properties have appeared.[16,18] In this communication we describe the deposition of titanium silicon oxide films onto Si(100) by the simultaneous thermal CVD of TiO_2 and SiO_2 and note the dramatic impact that the precursor structure plays in determining the film composition.

Tetraethyl orthosilicate (TEOS) was used as the source of silicon dioxide. Titanium tetraisopropoxide (TTIP) or anhydrous titanium tetranitrate (TN) was used to deposit the TiO_2 component. Precursors were purchased from Aldrich, and TEOS and TTIP were distilled under vacuum prior to use. All precursors were stored and the vessels were loaded under N_2. Substrates were cleaned using methylene chloride followed by a 7:3 solution of H_2SO_4 and 30% H_2O_2. Prior to deposition, a wafer was removed from this solution, rinsed thoroughly with deionized water, dipped into a 10% HF solution for 15 s, and blown dry with compressed air. The wafer was then immediately placed into the reactor, which was evacuated using a mechanical pump. The TEOS precursor vessel was cooled to 0 °C in an ice bath while the TN and TTIP vessels were warmed to 40 and 37 °C, respectively, using Variac-controlled heating tape. The high-purity N_2 flow rate was varied from 5 to 50 sccm through the TEOS vessel and from 5 to 100 sccm through the TN and TTIP vessels. Overall reactor pressures of 0.5−1.5 Torr were maintained during the process. The molybdenum susceptor was heated to the desired reaction temperature (300−535 °C) using a Variac-controlled 1000-W halogen lamp set within a parabolic, polished aluminum reflector. The TEOS vessel was opened first and allowed to equilibrate and then the TN or TTIP vessel was opened for the duration of the deposition.

Under all conditions no film growth was observed using TEOS alone. This was consistent with minimum temperatures of 650 °C reported for the thermal CVD of SiO_2[19,20] and with TPD studies showing no evidence of TEOS thermal decomposition on SiO_2 powders.[21] As TN or TTIP was introduced along with the TEOS, film growth of the mixed oxide was observed at rates ranging from 0.6 to 90 nm/min. Interruption of the TN or TTIP delivery (while maintaining the flow of TEOS) halted all film growth. Pure TiO_2 deposition continued after

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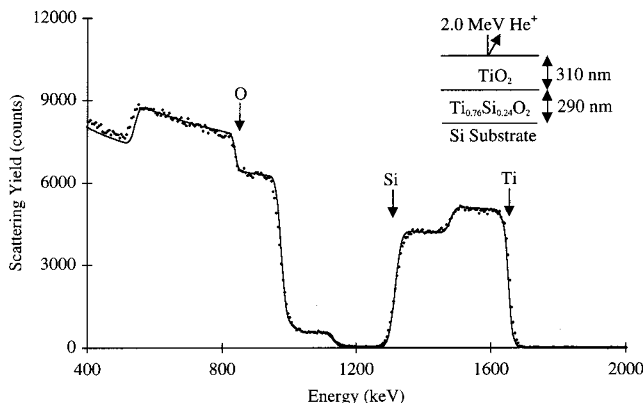

Figure 1. Rutherford backscattering spectrum of a film grown at 500 °C using TEOS (N_2 flow rate = 25 sccm) and TTIP (N_2 flow rate = 20 sccm). The TEOS vessel was closed after ≈250 nm of mixed oxide had grown. The model (solid line) corresponds to a 310-nm pure TiO_2 layer on top of a 290-nm layer with composition $Ti_{0.76}Si_{0.24}O_2$.

delivery of TEOS was stopped, as long as TN or TTIP flow continued.

The as-deposited films were amorphous to X-rays, and cross-sectional TEM showed no crystalline structure within the mixed oxide films or evidence of compositional inhomogeneity. At the interface between silicon and the $Ti_xSi_{1-x}O_2$ film a 1.4–1.8-nm interfacial layer was observed. This layer has been found in studies in which TiO_2 has been deposited on silicon[2,22–24] and has been identified as having a graded composition ranging from a SiO_2-rich zone at the silicon interface to a TiO_2-rich zone at the oxide interface. The formation of this layer could be due to exposure of the substrate to impurities in the gas at the beginning of the deposition or to an expected reaction[25] between TiO_2 and Si. Plan-view SEM images showed flat, featureless surfaces. Rutherford backscattering spectrometry confirmed the presence of both Ti and Si throughout the films. The spectra were modeled by compositions that corresponded to a mixture of titanium and silicon dioxide. Figure 1 shows the RBS spectrum for a film grown using TEOS and TTIP in which the TEOS vessel was closed after ≈250 nm of mixed oxide was deposited. The top layer corresponded to pure TiO_2, and the transition between the pure and mixed phases was sharp relative to the depth resolution of the RBS experiment.

The ratio of TiO_2 to SiO_2 was controlled by systematic variation of the carrier gas flow rate through the precursor vessels using the TTIP–TEOS precursor pair. For a growth temperature of 500 °C and a constant TEOS flow rate (10 sccm), Figure 2a shows that Ti:Si increased as the flow rate through the TTIP vessel increased from 5 to 100 sccm. Increasing the flow rate through the TEOS while maintaining a constant rate through the TTIP caused the relative TiO_2 content of the film to decrease. More research is necessary to establish whether the shape of these curves, in which

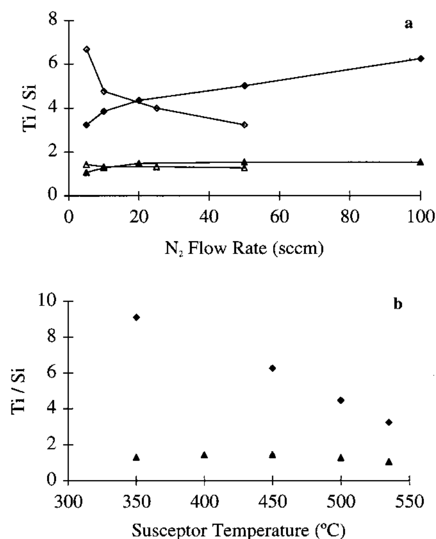

Figure 2. (a) Plot showing the dependence of the ratio of TiO_2 to SiO_2 on the carrier gas flow rate through the precursor vessels. Films grown using TN–TEOS are represented by triangles and films grown using TTIP–TEOS are represented by diamonds (hollow: TEOS 5–50 sccm and TN or TTIP 20 sccm; solid: TEOS 10 sccm and TN or TTIP 5–100 sccm). All depositions were performed at 500 °C. (b) Plot showing the dependence of the Ti:Si ratio on the deposition temperature. Carrier gas flow rates were 10 sccm through the TEOS vessel and 20 sccm through the TN or TTIP vessels. Films grown using TN–TEOS are represented by triangles and films grown using TTIP–TEOS are represented by diamonds.

the effect seemed to saturate at higher flow rates, was related to changes in transport phenomena or to deposition chemistry. While an independent measurement of the precursor partial pressures was not obtained, upper estimates based on the equilibrium vapor pressures (0.018 Torr for TTIP at 37 °C and 0.28 Torr for TEOS at 0 °C)[26] suggested that TEOS was always present in excess.

In striking contrast to the behavior of the TTIP–TEOS reactants, a similar variation in carrier gas flow rate produced virtually no change in the film stoichiometry in the TN–TEOS system. Under all conditions studied, the TiO_2:SiO_2 value remained close to unity.

Increasing temperature increased the deposition rate for both sets of precursors. In addition, the Ti:Si ratio of films grown using TTIP–TEOS monotonically decreased as temperature increased. For the TN–TEOS system, however, the Ti:Si value remained constant at all temperatures.

The binary phase diagram for the TiO_2–SiO_2 system does not indicate the presence of any unique phases.[27,28] At 500 °C limited solubility of one component in the other is observed; thus, the films produced in this study are not representative of equilibrium compositions. Annealing the films deposited from the TTIP–TEOS precursor combination at 600 °C for 2.5 h under N_2 resulted in crystallization of anatase. A similar thermal treatment of films grown from the TN–TEOS system (containing approximately equal TiO_2 and SiO_2 concentrations) did not result in any crystallization observable

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by X-ray diffraction. This behavior is most likely due to the excess TiO_2 that was present in all of the TTIP–TEOS grown films. In the TTIP–TEOS deposition system, the compositional variation reflects the deposition conditions in a systematic fashion. This is not the case when TN is used as the TiO_2 precursor. A plausible explanation would involve the existence of a specific chemical reaction between TN and TEOS during the early stages of deposition (either in the gas phase or on the surface). Recalling that TEOS is always present in excess and does not react by itself under these conditions, the impact of such a reaction would mean film stoichiometry could be controlled by the stoichiometry of the intermediate. Studies of the reactivity of anhydrous metal nitrates, including TN, established them as effective nitrating reagents; for example, alcohols react with TN to form organonitrates.[29] The proposed reaction of TEOS with TN, eq 1, is similar to the

$$Ti(OEt)_4 + Ti(NO_3)_4 \rightarrow TiO_2/SiO_2 + 4EtONO_2 \quad (1)$$

reaction of ROH with TN and would explain the 1:1 composition of films grown with this combination of precursors. The thermal instability of ethyl nitrate may preclude its observation during deposition at the temperatures used in this study. To explore the efficacy of this reaction, $Si(OEt)_4$ was mixed with a CCl_4 solution of $Ti(NO_3)_4$. After 30 min at room temperature, an amorphous white powder formed and, on the basis of ICP-MS, exhibited a Ti:Si ratio of 1.09. Proton NMR spectroscopy of the CCl_4 solution indicated the formation of resonances at 4.52 and 1.40 ppm attributable to ethyl nitrate. It is noteworthy that $TiO_2 \cdot 4SiO_2$ powders have been prepared in which the composition correlated with the stoichiometry of the precursor, $Ti[OSi(O\text{-}t\text{-}Bu)_3]_4$.[30] In addition to its relevance to the CVD process, eq 1 may have value as an alternative, low-temperature, nonaqueous route to $Ti_xSi_{1-x}O_2$ powders.

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