Thin Solid Films 519 (2010) 270–275

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Atomic layer deposition of SiO_2 from Tris(dimethylamino)silane and ozone by using temperature-controlled water vapor treatment

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ARTICLE INFO

Article history:
Received 12 May 2009
Received in revised form 22 July 2010
Accepted 23 July 2010
Available online 3 August 2010

Keywords:
Atomic layer deposition
Silicon dioxide
Adsorption
Infrared absorption spectroscopy
Ozone
Water vapor

ABSTRACT

Atomic layer deposition of SiO_2 from tris(dimethylamino)silane (TDMAS) and ozone as precursors on Si (100) surfaces at near-room temperatures was studied by infrared absorption spectroscopy with a multiple internal reflection geometry. TDMAS can be adsorbed at OH sites on hydroxylated Si surfaces at room temperature. Ozone oxidation of the TDMAS-treated Si surface is effective in removing hydroaminocarbon adsorbates introduced during TDMAS adsorption at room temperature. After oxidation by ozone, treatment with H_2O vapor at a substrate temperature of around 160 °C causes regeneration of OH sites for TDMAS adsorption. Cycles involving TDMAS adsorption and ozonization at room temperature followed by H_2O treatment at 160 °C permit the buildup of layers of SiO_2. The amount of residual hydroaminocarbon at the interface between the growing SiO_2 film and the substrate can be reduced with the ozone treated Si surface as a starting surface.

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1. Introduction

Sizes of semiconductor devices in large-scale integration (LSI) have reached the submicron range where gate oxide films in metal oxide semiconductor (MOS) devices need to be fabricated at a nanometer scale. Atomic layer deposition (ALD) is a technology for depositing dielectric films with monolayer precision by repeated cycles of saturating adsorption of source gases on a substrate that is subsequently reactivated for further adsorption. With respect to gate oxide film deposition, ALD of Si from $SiCl_4$ [1] or tetraethyl orthosilicate (TEOS; tetraethoxysilane) [2] as a precursor in the presence of an oxidizing gas has been reported. Tris(dimethylamino)silane (TDMAS; *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylsilanetriamine) could also be expected to act as a precursor for ALD of SiO_2 and silicate on Si [3], as it is easily vaporized and reacts readily with oxidants at room temperature. To control the ALD of SiO_2 from TDMAS with atomic precision, it is important to analyze the fundamental processes that are involved in adsorption and oxidization of TDMAS on Si surfaces.

We previously reported [4] on our direct observations of TDMAS adsorption and ozone oxidation on a Si (100) surface by means of multiple internal reflection (MIR) infrared absorption spectroscopy (IRAS). We found that TDMAS is dissociatively adsorbed on the Si (100) surface where it produces adsorbates that include hydroaminocarbons and Si hydrides, even at room temperature. IRAS showed that TDMAS adsorbs preferentially at OH sites on hydroxylated Si surfaces. The chemisorbed TDMAS on the Si surface can be oxidized by ozone, even at room temperature. However, when we used thermally cleaned Si (100) as a substrate, we found that a proportion of the hydroaminocarbon introduced during the first TDMAS adsorption remained at the interface between the growing SiO_2 and the substrate. The IRAS studies also suggested that continuous regeneration of OH sites on the surface is necessary to sustain cyclic growth of SiO_2. In the present work, we developed a process for regeneration of OH sites by using H_2O vapor and a temperature-controlled substrate. In this process, control of the substrate temperature between 155 and 160 °C was effective in sustaining the surface density of OH sites. IRAS also confirmed that the adsorption of TDMAS and sequential treatment with ozone and H_2O vapor enabled cyclic ALD of SiO_2 at near-ambient temperatures. We found that ozone treatment of the cleaned Si (100) surface before the first adsorption of TDMAS reduced the amount of residual hydroaminocarbon at the interface between the growing SiO_2 film and the substrate. Here we describe our experimental results and discuss how to achieve high-quality SiO_2 ALD at near-ambient temperatures.

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doi:10.1016/j.tsf.2010.07.107

2. Experimental details

A B-doped Si (100) substrate with a resistivity of approximately 10 Ω cm was used as a sample. The samples were introduced into an ultrahigh-vacuum (UHV) chamber with facilities for IRAS. Before introducing the sample into the chamber, the sample was cleaned by the standard RCA method [5] and then dipped in hydrofluoric acid (HF) to remove native oxide from the surface [6]. A schematic for the analytical chamber is given in Ref. [7]. The base pressure of the chamber was around 1.3×10^{-7} Pa. The sample surface was cleaned by resistive heating to 1050 °C for 2 min in an ultrahigh vacuum of 6.7×10^{-7} Pa. TDMAS and ozone exposures are given in Langmuir units ($1\ \mathrm{L}=10^{-6}$ Torr s $=1.33\times10^{-4}$ Pa s), as calculated from the product of the pressures of the gas, monitored with an uncalibrated ionization gauge, and the time.

The chemical state of the sample surface was monitored by MIR-IRAS in the analytical chamber. This technique is quite surface sensitive and has a higher energy resolution than do other spectroscopic tools, such as electron energy loss spectroscopy. The samples used for the MIR-IRAS measurements measured $0.5\times10\times40\ \mathrm{mm}^3$ with 45° bevels on each of the short edges. IR radiation from an interferometer (BOMEM MB-100) was focused at normal incidence onto one of the two bevels of the sample; it then propagated through the sample, reflecting internally about 80 times [8,9]. The IR radiation that exited from the other bevel of the sample was focused onto a liquid nitrogen-cooled InSb detector. Below, we discuss the changes in surface atomic structure during the ALD processes of precursor adsorption, ozone oxidization, and H_2O vapor treatment, as identified by IRAS. To calculate a particular IR absorption spectrum, we first recorded an IR transmission spectrum before the process as a base spectrum and then we recorded a second IR transmission spectrum after the process. If I_0 and I_r are the IR transmittances before and after the process, respectively, the absorbance (A_{bs}) can be calculated from the equation $A_{bs}=\log_{10}(I_r/I_o)$. The absorbance spectrum indicates only the change from the state before the process to that existing after the process. Similar analyses can be found in other papers on MIR-IRAS [8,9].

To show that SiO_2 ALD occurred, we measured the thickness and the breakdown voltage of the deposited SiO_2 film by means of X-ray photoelectron spectroscopy (XPS) and current–voltage (I–V) measurements, respectively. In the XPS measurements, we used an Alkα X-ray source with an electron energy of 1486.6 eV and we recorded photoelectrons with a take-off angle of 90° to the sample surface. For the I–V measurement, we fabricated 20 MOS capacitors with the deposited SiO_2 films, p-type, 10-Ω cm Si (100) substrates, and Au metal; we took the breakdown voltage as being the applied bias between the metal and the substrate at which the leakage current density reached $10^{-7}\ \mathrm{A/cm}^2$. In this measurement, a positive bias was applied to the substrate and the metal was connected to ground to avoid hole depletion in the Si substrate, which would otherwise have enhanced the breakdown voltage.

3. Results and discussion

First, we confirmed by means of MIR-IRAS measurements that TDMAS adsorbs onto a thermally cleaned Si (100) surface. The results are shown in Fig. 1. The background spectrum for the calculation of the absorbance spectra of the Si(100) surface with adsorbed TDMAS was recorded immediately after thermal cleaning. The exposure (see above) of the Si(100) to TDMAS ranged from 0.6 to 18667 L. In the low-exposure range below 16 L, two IR absorbances occurred at 3676 and 2073 cm^{-1}, which we attributed to hydrogen-bonded OH and SiH, respectively [10,11]. We consider

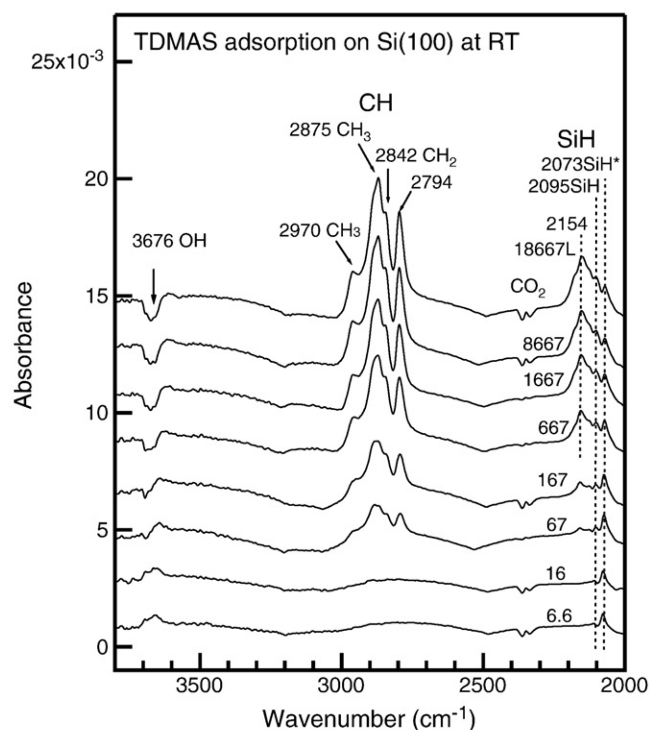
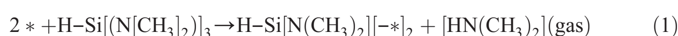


Fig. 1. MIR-IR spectra of TDMAS adsorbed on Si(100) surfaces at various exposures from 0.6 to 18667 L.

that these species were introduced by adsorption of H_2O remaining in the analytical chamber. Although we used an UHV chamber with a base pressure of 1×10^{-7} Pa, the adsorption of H_2O was unavoidable because H_2O molecules have a high sticking coefficient of 1.0 on cleaned Si surfaces [12]. TDMAS adsorbs on the Si surface to form C–H and hydroaminocarbon species, the presence of which is shown by absorbances in the range 2800–3000 cm^{-1} at exposures exceeding 67 L. The C–H peak is split into four peaks; the peaks at 2875 and 2960 cm^{-1} are attributed to CH_3 groups, whereas the peaks at 2858 and 2929 arise from CH_2 groups [9]. A sharp peak at 2800 cm^{-1} was attributed to dimethylamine groups $[N(CH_3)_2]$. We consider that all the C–H peaks arise from $N(CH_3)_2$ moieties in the TDMAS molecules adsorbed on the Si surface. In our previous study [4], the IR absorbance of Si–H in isolated TDMAS molecules was seen at 2119 cm^{-1}. As shown in Fig. 1, the SiH peaks in the IR absorbance spectra are blue shifted; for the present, we assume that this is a result of dissociative adsorption of TDMAS as $H{-}Si[N(CH_3)_2][{-}O{-}Si(bulk)]_2$. This view is supported by an analysis of the number of adsorption sites, as discussed below.

In the IR absorption spectrum of Si (100) with adsorbed TDMAS (Fig. 1), there is a decrease in the absorbance at 3676 cm^{-1}. This is caused by the degeneration of hydrogen-bonded Si–OH in the adsorption, which suggests that Si–OH plays a role as an adsorption site for TDMAS. We therefore believe that TDMAS is dissociatively adsorbed on the H_2O-adsorbed Si(100) surfaces in the a form of $H{-}Si[N(CH_3)_2][{-}O{-}Si(bulk)]_2$ as shown in the following scheme:



$$2*+H{-}Si[(N[CH_3]_2)]_3\rightarrow H{-}Si[N(CH_3)_2][-*]_2+[HN(CH_3)_2](gas) \quad (1)$$

where * represents an adsorption site. We also consider that, besides Si–OH, a dangling bond is also a possible adsorption site. In this reaction, we assumed that adsorption of TDMAS on the surface consumes two adsorption sites. If we assume single-site

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