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Ultrathin tunnel insulator films on silicon for electrochemiluminescence studies

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ABSTRACT

Thin insulating films on conductive substrates have been used for tunnel emission of hot electrons into aqueous solution. The hydrated electrons thus formed induce electrochemiluminescence (ECL) in various luminophores, e.g. rare-earth metal chelates, which can be detected in sub-nanomolar concentrations. The luminophores can be used as labels for antibodies, enabling simple and highly sensitive immunoassays. This paper compares thermal silicon dioxide, low pressure chemical vapor deposited silicon nitride, plasma enhanced chemical vapor deposited silicon dioxide and nitride, atomic layer deposited alumina, and liquid phase deposited silicon dioxide for electrodes in ECL applications.

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1. Introduction

Hydrated electrons are an effective way of producing various electrochemical reactions e.g. electrochemiluminescence in aqueous solution. Traditionally they are formed by photoemission or pulse radiolysis, but a more convenient method for microanalytical systems and point-of-care analysis is tunnel emission from insulating film-covered electrodes by cathodic pulse polarization. The effect is similar to metal/insulator/metal tunneling [1,2] and tunnel emission of electrons into vacuum [3,4].

Hot electron-induced electrochemiluminescence (HECL) is a sensitive and selective method for determining luminophores, including several rare-earth chelates, in nanomolar to picomolar concentration. In previous work, high-conductivity silicon electrodes covered by 2–6 nm of silicon dioxide [5,6], as well as aluminum electrodes covered by aluminum oxide [7,8], have been used to emit electrons into solution to produce HECL. High selectivity is attained by using optical filters for spectral discrimination, and sensitivity is further improved by measuring luminescence in a time-resolved manner, to observe only the long-lived luminescence of the desired species excited by hydrated electrons [9,10]. By using the luminophores as labels for antibodies, HECL can be used in immunoassays [11].

In this work we have studied the application of silicon dioxide, silicon nitride and aluminum oxide as working electrode dielectrics

for HECL. The films were prepared by various methods, including thermal oxidation, atomic layer deposition (ALD), chemical vapor deposition (CVD) and liquid phase deposition (LPD). The effect of film thickness on HECL signal intensity was investigated for the various types of film.

2. Experimental methods

Highly conductive *n*-type silicon wafers of 0.005–0.018 Ω cm resistivity and (111) orientation were used as the working electrode substrates. The wafers were initially RCA-cleaned (10 min 1:1:5 solution of 25% $\text{NH}_4\text{OH} + 30\% \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ at 80 °C, 30 s 1:5:5 solution of 50% $\text{HF} + \text{H}_2\text{O}$ at room temperature, and 15 min 1:1:5 solution of 37% $\text{HCl} + 30\% \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ at 80 °C), and dipped in HF immediately prior to all film depositions (except liquid phase deposition) to remove native oxide from the silicon surface. Film thicknesses were measured with a Philips SD 2300 ellipsometer operating at 632.8 nm wavelength using a fixed refractive index (bulk values obtained from the literature: 1.465 for SiO_2 , 2.021 for Si_3N_4 and 1.766 for Al_2O_3), as the refractive index cannot be reliably determined from such thin films.

Thermal silicon dioxide was grown in a Centrotherm oxidation furnace at 850 °C in a 10% oxygen, 90% nitrogen atmosphere. A full RCA-cleaning process was performed immediately prior to oxidation, with the additional HF dip last. An oxidation time of 20 min yields approximately 4 nm of oxide.

Silicon nitride was deposited in a Centrotherm low pressure CVD (LPCVD) furnace using a standard recipe of 40 sccm dichlorosilane and 200 sccm ammonia at 250 mTorr (33 Pa) pressure and 770 °C

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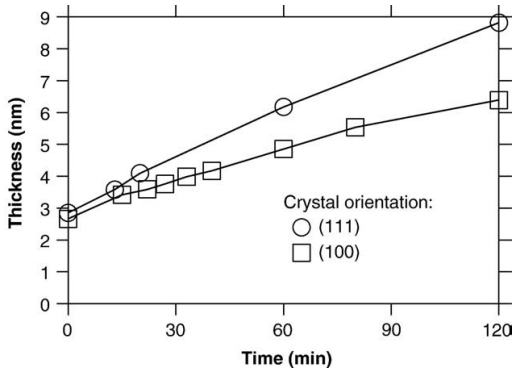


Fig. 1. Thermal oxide thickness versus oxidation time at 850 °C temperature in a 10% oxygen atmosphere.

deposition temperature. With a deposition time of only 1 min, about 5 nm of silicon nitride was obtained.

Plasma enhanced CVD (PECVD) of silicon dioxide and silicon nitride were carried out in an Oxford Plasmalab 80 Plus single-wafer reactor using standard recipes with reduced RF power and silane flow. The films were deposited at 300 °C and 1000 mTorr (130 Pa) pressure with 5 W RF power. The reactant gas flows were 2.0 sccm SiH₄, 710 sccm N₂O and 161.5 sccm N₂ for silicon dioxide, and 20 sccm SiH₄, 30 sccm NH₃ and 380 sccm N₂ for silicon nitride.

Aluminum oxide was grown by atomic layer deposition in a Beneq TFS-500 reactor at 220 °C temperature and approximately 5 mbar (500 Pa) pressure, using trimethyl aluminum and ozone as precursors. Ozone was used as the oxygen precursor instead of the more common water, as it initiates growth faster on bare silicon whose native oxide has been removed [12]. The observed growth rate was approximately 0.1 nm per cycle.

Liquid phase deposition of silicon dioxide was carried out from SiO₂-saturated hexafluorosilicic acid (H₂SiF₆) solution by addition of water and boric acid (H₃BO₃) at 35 °C temperature, as detailed in [13]. Deposition was performed on silicon substrates with the surface chemically oxidized in RCA-cleaning, since deposition does not occur with this method if the native oxide has been removed. Deposition times varied from 2 to 20 min.

HECL-measurements with the prepared working electrodes were carried out in an 8 mm diameter sample cell with a platinum wire counter electrode. Coulostatic pulses were applied with an in-house built pulse generator, and luminescence was measured by photon counting as detailed in [14]. A total of 1000 pulses were measured in a time-resolved fashion, during a 6 ms measurement window following a 50 s delay, at a rate of 20 Hz. Tb(III) chelated by 2,6-bis[N,N-bis(carboxymethyl)aminomethyl]-benzoylphenol was used as the model luminophore. Data was collected separately from each pulse, to monitor the HECL signal stability over the entire measurement. All the data points were integrated to evaluate the overall performance of each electrode type.

3. Results

3.1. Film quality

Thermal silicon dioxide is known to be pinhole-free and of high quality down to the nanometer thickness regime. Its growth kinetics and reliability in this range have been studied extensively for complementary metal–oxide–semiconductor applications [15–17]. In the present study, thickness uniformity was confirmed to be excellent over the wafer as well as from wafer to wafer. Ellipsometer measurements had a standard deviation between 0.4% and 0.9% of film

thickness both across the wafer, as well as wafer to wafer. Film thickness on (111) as well as (100) wafers can be accurately controlled by varying the oxidation time (Fig. 1). Native oxide is stripped immediately prior to oxidation, but some oxide is grown already during the wafer loading and temperature ramping stages.

LPCVD silicon nitride thickness was determined by ellipsometry to be uniform across the wafer despite the short deposition time. The measured standard deviation was between 1.5% (shortest deposition times) and 0.5% (longest deposition times). A slight decreasing trend was observed towards the loading end of the furnace, between 1% and 2.5% wafer to wafer, being again most pronounced for the shortest deposition times. The film thickness was found to be nearly linear in relation to deposition time (Fig. 2).

To test the Si₃N₄ film for pinholes, a 1 minute LPCVD deposition (5 nm thickness) was performed on samples coated with thick silicon dioxide, followed by etching in HF-based SiO-Etch solution. The etch rate of silicon nitride in SiO-Etch was 1 nm/min, whereas thermal oxide etches at >100 nm/min. After 2 min of etching, no discoloration or texturing of the underlying oxide layer was evident in optical microscope inspection, indicating the film to be pinhole-free. However, silicon nitride samples deposited on bare silicon displayed a greatly increased etch rate in the last nanometer of material. This indicates the presence of a native oxide layer formed under the deposited nitride, presumably during the loading, pumping and temperature ramping phases of the deposition process. This also agrees with the measured thickness data of Fig. 2. Extrapolating the thickness data to zero deposition time suggests that the native oxide thickness is about 2 nm.

Silicon dioxide and silicon nitride films deposited by PECVD, as well as LPD silicon dioxide films all differ in composition and morphology from known high-quality films grown by oxidation or LPCVD. Due to the low deposition temperatures, they contain dangling bonds as well as various reaction products from the deposition process. These factors lead to extremely high observed etch rates in HF-based etchants. The measured etch rates of PECVD silicon nitride and silicon dioxide in SiO-etch solution were 5× and over 20× that of thermal oxide, respectively.

Ultimately thin ALD films e.g. hafnium oxide have been extensively researched for high-κ dielectric applications [18]. Plasma etching studies have shown ALD alumina to be likewise continuous and pinhole-free already below 10 growth cycles (1 nm) [12].

3.2. HECL

Luminescence signals using 10^{−6} mol/dm³ Tb(III) chelate as the model luminophore were measured for various film thicknesses of the

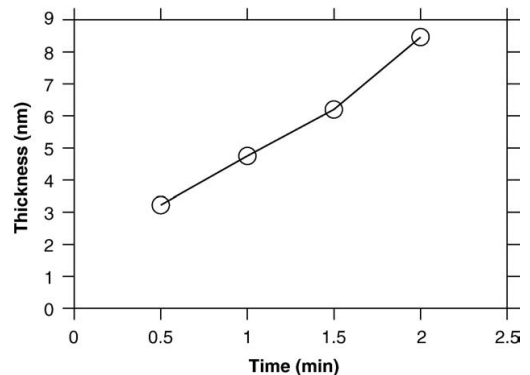


Fig. 2. Measured thickness of silicon nitride versus deposition time using a standard LPCVD process. A layer of native oxide at the Si/Si₃N₄ interface may affect the ellipsometer results.

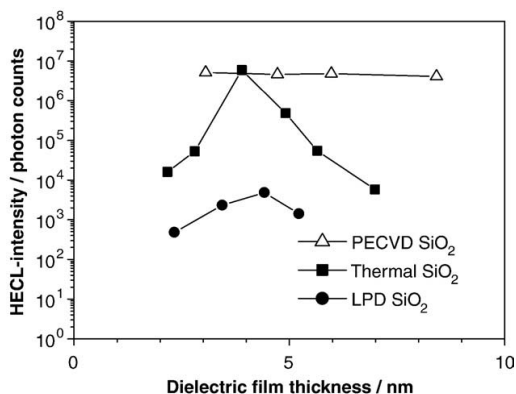


Fig. 3. Observed HECL signal intensity using different thicknesses of thermal and deposited silicon dioxide as the tunneling dielectric.

different dielectric materials. Figs. 3 and 4 present the results, integrated over all 1000 measurement pulses. All measurements were performed in time-resolved fashion. Thermal silicon dioxide shows the sharpest optimum at approximately 4 nm thickness. Other materials also tend to peak in the same thickness range. Overall best results are obtained with thermal silicon dioxide, LPCVD silicon nitride, ALD alumina and, surprisingly, PECVD silicon dioxide.

Figs. 5 and 6 present the individual photon counts from consecutive measurement pulses, obtained using the optimum thickness of each film. As can be seen, both thermal and PECVD silicon dioxide, as well as LPCVD silicon nitride, are extremely stable over the entire measurement. PECVD silicon nitride and ALD alumina produce a significant signal, which, however, varies over the course of the measurement. This variation is highly recurrent from one sample to another, *i.e.* the highest signal is always observed during the same measurement pulses. It may therefore be feasible to increase signal-to-noise ratio by integrating data collected only from such high-signal windows, *e.g.* pulses 50–200 for PECVD silicon nitride in Fig. 6. LPD silicon dioxide produces little or no signal after 10 pulses, and is therefore practically unusable.

Calibration plots of HECL intensity versus luminophore concentration are produced from data integrated over multiple measurement pulses in order to reduce noise. Fig. 7 presents such a calibration plot, measured using a silicon working electrode coated with 3.8 nm ALD-deposited Al₂O₃. The baseline signal of approximately 10³ counts, obtained at zero concentration, has been subtracted from the data.

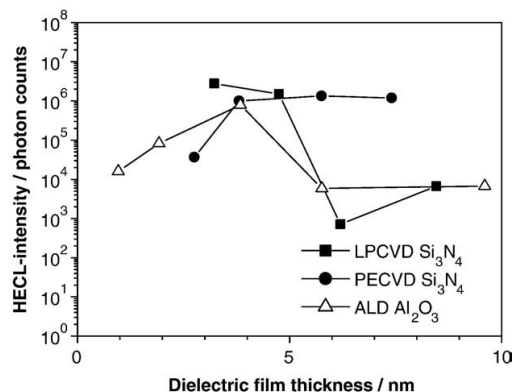


Fig. 4. Observed HECL signal intensity using different thicknesses of silicon nitride and alumina as the tunneling dielectric.

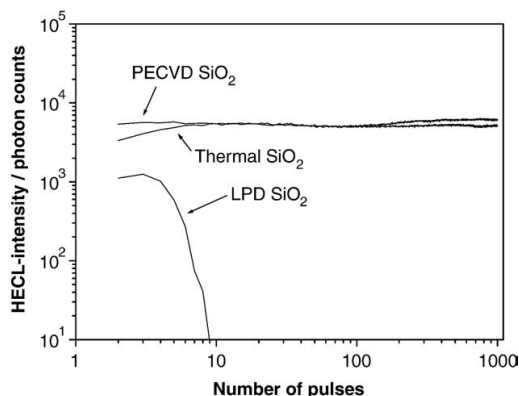


Fig. 5. Behavior of silicon dioxide films over consecutive measurement pulses, measured using 10⁻⁶ M Tb(III) chelate.

The plot shows good linearity and sensitivity down to nanomolar concentration.

The stability of HECL electrodes over time is very good. Samples have been measured with the model luminophore after several months of storage. No degradation in performance has been observed, when compared to identical samples measured immediately after deposition.

4. Conclusions

All three materials tested (silicon dioxide, silicon nitride and aluminum oxide) were demonstrated to work as tunnel dielectrics on highly conductive silicon, and are therefore useful in HECL applications. It may be surmised that a multitude of other dielectrics work as well. However, the deposition method and the resulting overall film quality are critical.

Thermal silicon dioxide, LPCVD silicon nitride and ALD alumina are known to be high-quality films, and also perform well as tunneling dielectrics in HECL applications. Rather surprisingly, PECVD silicon dioxide also performs well, with high signal and excellent stability over the entire measurement. Possibly the high ratio of N₂ and N₂O to SiH₄ during deposition leads to oxynitride formation. Plasma deposited oxynitrides have been used as tunneling dielectrics in non-volatile memory applications [19,20], and oxynitride formation has

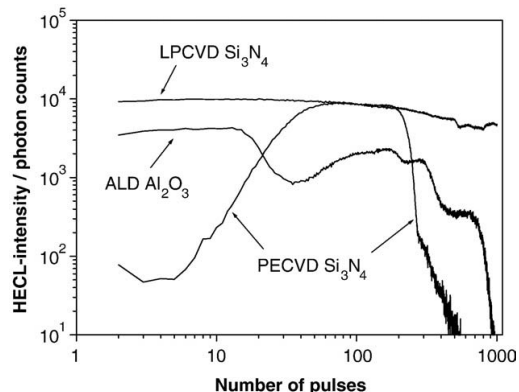


Fig. 6. Behavior of silicon nitride and alumina films over consecutive measurement pulses, measured using 10⁻⁶ M Tb(III) chelate.

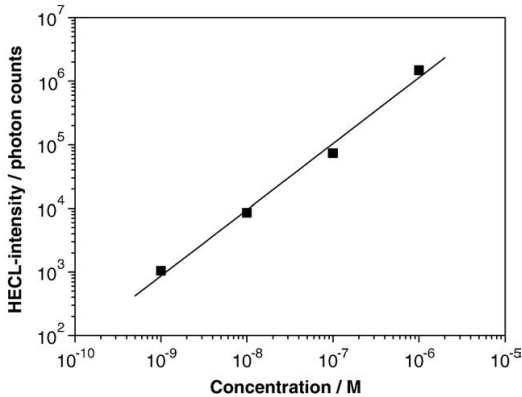


Fig. 7. A calibration curve for Tb(III) chelate using a 3.8 nm Al_2O_3 covered silicon working electrode.

also improved the performance of CVD gate dielectrics in metal-oxide-semiconductor devices [21,22].

PECVD silicon nitride, on the other hand, gives an overall lower signal. It may also be usable if the signal is integrated only between 50 and 200 pulses where the signal is strongest. This high-signal window is repeatable from sample to sample. Silicon dioxide deposited by LPD, a room temperature process, does not work in any practical way. The signal is very low and diminishes completely after the first few measurement pulses.

The sensitivity of HECL combined with spectral discrimination and time-resolved detection is very good. Sub-nanomolar concentrations can be detected, and calibration plots remain highly linear over several orders of magnitude.

Having a variety of different insulator materials to select from will be important when binding antibodies to the electrode surface for

immunoassays. Since deposited materials are found to work as well as thermally oxidized silicon, a wide variety of other substrate materials is possible as well. The low process temperatures possible by using ALD alumina or PECVD silicon dioxide as dielectrics are advantageous for integration of HECL sensors and other devices on the same chip.

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