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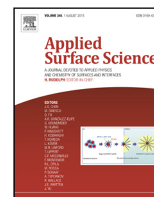

Nucleation and initial growth of atomic layer deposited titanium oxide determined by spectroscopic ellipsometry and the effect of pretreatment by surface barrier discharge

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ABSTRACT

This paper reports on the use of spectroscopic ellipsometry to characterise the initial nucleation stage of the atomic layer deposition of the anatase phase of titanium dioxide on silicon substrates. Careful control and analysis of the ellipsometric measurements enables the determination of the evolution of crystallite diameter and surface density in the nucleation stage before a continuous film is formed. This growth behaviour is in line with atomic force microscopy measurements of the crystallite size. The crystallite diameter is a linear function of the number of ALD cycles with a slope of approximately 1.7 Å $cycle^{-1}$ which is equivalent to a layer growth rate of 0.85 Å $cycle^{-1}$ consistent with a ripening process which increases the crystallite size while reducing their density. The crystallite density decreases from $\sim 3 \times 10^{17}$ m^{-3} in the initial nucleation stages to $\sim 3 \times 10^{15}$ m^{-3} before the film becomes continuous. The effect of exposing the substrate to a diffuse coplanar surface barrier discharge in an air atmosphere before deposition was measured and only small differences were found: the plasma treated samples were slightly rougher in the initial stages and required a greater number of cycles to form a continuous film (∼80) compared to the untreated films (∼50). A thicker layer of native oxide was found after plasma treatment.

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1. Introduction

Dielectric barrier discharges (DBDs) are widely used for modification of various surfaces in order to passivate them, change their surface energy or modify the deposition behaviour of layers deposited on them [1–3]. DBD plasma sources have good process controllability, excellent treatment uniformity and high efficiency. Plasma treatment of substrates can generate various functional groups on the surface of materials such as hydroxyl-, carbonyl-, carboxyl-, amino-groups, etc.

Atomic layer deposition (ALD) is a thin film deposition process known for its ability to controllably deposit ultrathin layers with extreme uniformity. In ALD, the substrates are exposed to sequential pulses of reactant gases or vapours and each pulse forms an additional chemisorbed molecular layer. Between the reactant pulses, an inert gas (e.g. nitrogen) is used as a purge gas for removing all the excess precursor molecules which have not chemisorbed or undergone exchange reactions with the surface groups, and the reaction by-products [4]. It is widely accepted [5–8] that during ALD growth, the high density of active surface groups generated by plasma oxidation of a precursor monolayer can play an important role since during the subsequent precursor exposure these groups react with the incoming compounds which thereby become anchored. However, during the initial nucleation stage, where a precursor must react with the oxidised silicon substrate rather than a monolayer of the previous precursor, the action of the plasma on the silicon may not have such a significant effect.

Once the deposition process has reached a stable condition, the thickness of the films deposited by ALD is normally assumed to be strictly proportional to the number of ALD cycles applied. However, this requires that the film is dense and uniform and clearly

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cannot hold for the period from the initial nucleation until a coherent film is formed. During this time, growth typically proceeds by the formation of a certain surface density of nuclei followed by their expansion and eventual coalescence into a continuous film in a Volmer-Weber process [9]. The amount of material deposited during growth can be measured by deposition on a quartz crystal microbalance but this only gives the mass of material deposited. It does not give any information about the nucleation density or the continuity of the film. Ellipsometry can also be used to measure film thickness but, again, this works best for thicker, continuous films. In order to determine the growth rate of crystallites and the number of cycles necessary to form a continuous film, transmission electron microscopy can be used. This needs careful and time-consuming sample preparation and cannot be done on large samples.

Nanocrystalline films exhibit optical behaviour which differs from that of the bulk macrocrystalline material. This is predominantly due to quantum confinement (QC) effects [10] which come into play for crystallite diameters less than the Bohr radius. These effects have been reviewed by Trindade for a variety of semiconductors [11]. The optical absorption edge provides a simple way of observing these effects since QC causes it to be shifted to shorter wavelengths. Previous work [12] has shown that in thin titanium dioxide layers grown by ALD, the film thickness could be correlated with the effective quantum dimension calculated from the bandgap shift caused by QC. The band edge was estimated using the extinction coefficient data obtained by spectroscopic ellipsometry (SE). The current paper shows that measurement of the combination of thin film thickness and surface roughness by SE can not only measure the parameters of continuous films but can also detect the presence of discontinuous films composed of nanocrystallites. It identifies the number of ALD cycles at which the isolated crystallites combine into a continuous film and shows that the crystallite size and surface density can be obtained in this initial growth regime. The optical bandgap is estimated from the increase in extinction factor at short wavelengths and, once the bandgap is known, the crystallite diameter can be estimated from theoretical considerations. Using this calculated diameter, in a process explained below, we can estimate the crystallite density on the substrate and find how it varies with the number of ALD cycles.

This technique is applied to the nucleation and growth of ALD titanium dioxide on as-received silicon covered with a native oxide layer or on silicon which has been subject to a DBD treatment in air. The crystallite size and density and the number of cycles necessary to create a continuous film are compared between the two surface treatments.

2. Materials and methods

The substrates were Czochralski-grown boron-doped, single-side polished wafers of ⟨1 0 0⟩ silicon, obtained from Si-Mat (Germany). The silicon wafers were cut into approximately 15×15 mm samples and cleaned using an ultrasonic bath with acetone, isopropanol and deionized water consecutively, each with a time of 300 s. After cleaning, the substrates were dried using compressed air. Some were subject to a dielectric barrier discharge treatment in an ambient air atmosphere. In this case, a Diffuse Coplanar Surface Barrier Discharge (DCSBD) [13] type of dielectric barrier discharge was used. The DCSBD consists of many parallel stripline electrodes (1.5 mm in width; 1 mm in interelectrode gap) embedded in 96% alumina and is powered with peak to peak voltage up to 20 kV at frequencies from 14 kHz up to 18 kHz. The unique properties of DCSBD are based on generation of a visually diffuse low-temperature, nonthermal plasma with high power density up to 100 W cm^{-3} [14]. The plasma is generated in an approximately 0.3 mm thick layer on the surface of the dielectric ceramic. The DCSBD plasma source is described in more detail in Ref. [2]. The treatment of the silicon samples by DCSBD plasma was performed in a dynamic treatment mode, where the sample was moved through the plasma layer above the dielectric surface with defined speed and distance from the ceramic. The dynamic regime should provide homogeneous and uniform plasma treatment. The dynamic treatment system used is shown in Fig. 1. The power supplied to the DCSBD plasma system was 300–310 W equivalent to approximately 1.5 W cm^{-2}. The silicon samples were plasma treated for 5 s while the distance between the sample surface and the top of the ceramic surface was approximately 0.3 mm. The plasma treatment of silicon samples was carried out directly before they were loaded into the ALD system. These samples are identified in this paper as 'plasma treated' samples. The other samples without plasma treatment are labelled as 'untreated'. There are no other differences between these two types of samples.

The ellipsometry was carried out using a J.A. Woollam M-2000UI spectroscopic ellipsometer in the wavelength range of 210–1500 nm at angles of incidence of 65°, 70° and 75°. The data were analysed using WVASE software. The ellipsometric properties of the plasma treated and untreated silicon were measured after subjecting them to the same conditions as they would undergo before the start of the ALD process. That is, they experienced the same thermal history. They were also exposed to one cycle of the ALD process to ensure as far as possible that they replicated the properties of the substrate before any significant film growth. The ellipsometric properties of the substrates were then carefully measured to obtain accurate parameters for film thickness, optical parameters, etc. This is necessary if reliable measurements of deposited film thickness, roughness and optical constants are to be obtained. The process is described in more detail in Appendix A.

The titanium dioxide films were deposited using $TiCl_4$ (99.0% Fluka) and deionized water precursors in a Beneq TFS 500 ALD reactor. The reaction temperature was 350 °C and the pulse lengths of $TiCl_4$ and H_2O were 0.6 s and 0.25 s, respectively. Nitrogen (99.999%) was used as a carrier and purge gas with purging time 1 s after $TiCl_4$ exposure and 0.5 s after H_2O exposure. The chamber pressure was $\sim 2 \times 10^2$ Pa.

3. Results and discussion

The thickness of the ALD TiO_2 films appears to be a linear function of the number of ALD cycles, as expected. This is shown in Fig. 2a and b for the plasma treated and untreated samples, respectively. The roughness of the samples is also approximately a linear function of the number of cycles and is approximately 10% of the film thickness. However, if the graphs are expanded to look in more detail at the initial growth region there are some interesting features. Fig. 3a and b show the initial growth region.

No film growth can be detected for 3 (5) cycles for plasma treated (untreated) substrates. After growth begins, the ellipsometric modelling shows that the film thickness is zero and the roughness is greater than zero. This is consistent with there being no complete film formation on the substrate and growth taking place in isolated islands. The roughness increases with the number of cycles as would be expected if the islands were growing larger. An alternative explanation would be that there were a larger number of isolated islands being formed. The model for the surface roughness layer cannot distinguish between these two situations since it is based on an effective medium approximation which is 50% void and 50% film material. It is not possible to decouple the thickness and void content of this layer since they are correlated in the model fitting. It is clear, however, that there is no coherent film formation until between 50 and 100 ALD cycles have taken place. After this period, when the islands have coalesced to form a continuous

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