Studying Composition of Al$_2$O$_3$ Thin Films Deposited by Atomic Layer Deposition (ALD) and Electron-Beam Evaporation (EBE) upon Rapid Thermal Processing

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Abstract
This article discusses integrated analysis of composition of aluminum oxide layers deposited onto substrates of monocrystalline Si by atomic layer deposition (ALD) and electron-beam evaporation (EBE) using Auger spectroscopy and time-of-flight secondary ion mass spectrometry (ToF SIMS). Peculiar features of surface morphology and in-depth compositions of layers deposited by these methods upon rapid thermal annealing in argon environment were investigated. Detailed comparative specimens analysis of these procedures have been performed upon deposition of thick passivating layers of aluminum oxide on monocrystalline Si substrates before and after thermal post-processing. Possible reasons of the processes occurring in the considered structures upon thermal processing have been determined. Reasonability of deposition of atomic layer deposition of technological layers upon generation of passivating and antireflection coatings in photovoltaics has been substantiated.

Keywords: Al$_2$O$_3$ films, silicon plates, atomic layer deposition, electron-beam evaporation, Auger spectroscopy, time-of-flight secondary ion mass spectrometry, surface morphology, thermal annealing, element distribution profile.

INTRODUCTION
Nowadays surface passivation procedures become more and more important in production of high efficient solar cells. Substrate thickness is made thinner in order to decrease prime costs. While volume to surface area ratio decreases the surface recombination probability with numerous imperfections, namely dangling bonds, increases. Currently some materials for passivation on the basis of silicon are already studied, for instance, SiO$_2$, SiN$_x$, SiC and a-Si. Various deposition procedures of passivating coatings of various compositions are applied, in particular: chemical vapor deposition (CVD) [1], metalorganic chemical vapor deposition (MOCVD) [2], spray pyrolysis [3], thermal evaporation [4], magnetron sputtering [5]. In the latter procedure one of the most promising passivating materials is Al$_2$O$_3$.

Thus, in [6] aluminum oxide films were obtained by electron beam evaporation under ultrahigh vacuum. The authors studied microstructure, optical and dielectric properties of Al$_2$O$_3$ thin films as a function of substrate temperature and annealing temperature.

At the same time atomic layer deposition (ALD) of Al$_2$O$_3$ became a promising approach to researches due to superior passivating properties for Si of p- and n-type [7-8]. Such passivating properties are related with high negative charge which generates charged layer on Si surface in order to decrease recombination [9-11]. Al$_2$O$_3$ coatings deposited by ALD are characterized by extended charge lifetime and low rate of surface recombination on Si substrates of n- and p-type [12-15]. In addition it should be mentioned that ALD is based on the principles of precursor adsorption with its subsequent transformation in oxide, thus, the Al$_2$O$_3$ layer deposited on silicon substrates can decrease -surface imperfections density of silicon crystalline structure. Such decrease in the surface imperfections density is also related with high passivation level of aluminum oxide.

However, production of solar cells involves high temperature procedures upon formation of metal contacts. These procedures can impair passivating properties of aluminum oxide layers. Thus, some works were published devoted to investigations into degradation and imperfections occurrence of Al$_2$O$_3$ passivating layers after thermal processing [16-17].

This article investigates into peculiar features of composition variations of Al$_2$O$_3$ thin films deposited onto monocrystalline Si substrates by ALD and electron beam evaporation upon rapid thermal processing.

EXPERIMENTAL
In both cases silicon plates Si (100) with the diameter of 100 mm were used as substrates with the layer native oxide SiO$_2$. Deposition was carried out by ALD and electron beam evaporation.

Deposition of aluminum oxide by atomic layer deposition was carried out on a QT-ALD 250 facility of our own design. The temperature in reaction chamber was maintained at 200°C. Trimethylaluminum (TMA, Sigma-Aldrich) and deionized water were used as precursors maintained at ambient temperature. Nitrogen was used as carrier and purging gas. The following parameters were applied as optimum deposition mode:

- Temperature of working chamber: 200°C;
- Vacuum range in working chamber: 0.01-0.1 mbar;
• Duration of TMA feeding into reactor: 0.5 s;
• Duration of water injection into reactor: 0.3 s;
• Duration of purging: 5 s;
• Nitrogen consumption upon purging: 0.6 l/min;
• Number of cycles: 200.

Deposition of aluminum oxide by electron beam evaporation was carried out on an Angstrom EvoVac facility with the following process variables:

• Pressure in vacuum chamber: 2.6×10⁻³ mbar;
• Cleaning was performed by Ar⁺ ions in 30 seconds;
• Substrate temperature: 20°C;
• Sapphire plates were used as sputtering material.

Thermal processing was carried out on an AS-One rapid thermal annealing (RTA) facility (ANNEALSYS, France). Annealing was performed at 800°C and 1000°C in argon environment in 5 min. Heating rate was 20°C/s.

Profile analysis of composition and structure of the obtained Al₃O₅ films before and after thermal processing was performed by Auger spectroscopy using a PHI-670 xi Physical Electronics spectrometer and by time-of-flight secondary ion mass spectrometry using a ToF-SIMS.5 instrument.

Profile analysis by Auger spectroscopy was carried out at the accelerating voltage of primary electron beam of 5kV, primary current of 10 nA at the surface of ~0.75 ± 100 µm in order to prevent artifacts of electron beam impact on specimen (reduction of oxide, interlayer diffusion, and so on). Sputtering upon profile analysis was performed by Ar⁺ ions with the accelerating voltage of 2 kV, current of 0.5 µA at 30° to specimen surface. Herewith, the ion beam was unfolded into a raster of 1.5×2 mm (in order to adjust sputtering rate). Concentration of elements was calculated according to the model of homogeneous distribution using relative coefficients of reverse element sensitivity. The element sensitivity coefficients were determined by reference specimens analysis: sapphire plates and high temperature SiO₂ on Si.

Time-of-flight secondary ion mass spectrometry was performed using a ToF-SIMS.5 instrument. Analysis was performed by Bi ions. Layer-by-layer etching was performed by Cs ions. Accelerating etching voltage of 500 V was selected as optimum parameter for in-depth resolution, since in such etching mode additional relief propagation does not occur. Etching area was 300×300 µm. Analysis area: 100×100 µm. Such parameters were selected in order to eliminate the influence of etching crater walls on final result.

Recalculation of etching time to the depth was performed after depth measurement of ion etching crater using an Alpha-Step D-120 KLA Tencor stylus profilometer.

RESULTS AND DISCUSSION

In both cases the thickness of deposited aluminum oxide films about 20 nm.

Figure 1 illustrates the profiles of element in-depth distribution in initial Al₃O₅ films deposited onto monocrystalline Si plate by ALD and electron beam evaporation obtained by Auger spectroscopy.

![Figure 1](image-url)
thickness increasing of this oxidized layer. On ALD samples the thickness of this layer at equal annealing temperatures is more than by 1.5 times lower than on the Al₂O₃ samples formed by electron beam evaporation.

Figure 2 illustrates the images of deposited films surfaces in secondary electrons of Al₂O₃ films of both types before and after annealing.

**Figure 2.** SEM images of surface of Al₂O₃ films deposited onto monocrystalline Si plate by ALD (a, c, e) and electron beam evaporation (b, d, f) before (a, b) and after (c-f) thermal annealing at 800°C (c, d) and 1000°C (e, f).
As it can be seen from the presented images the surface of initial samples is very smooth. However, upon thermal processing variations of surface morphology can be observed. While comparing these variations it is obvious that the film structure upon rapid annealing varies differently.

The detected variations were analyzed by Auger spectroscopy in element distribution profiles of Al₂O₃ films obtained by ALD and electron beam evaporation after annealing at 800°C and 1000°C (Fig. 3).

**Figure 3.** Element distribution profile obtained by Auger spectroscopy in Al₂O₃ films after annealing at 800°C (a, b) and 1000°C (c, d) generated by ALD (a, c) and electron beam evaporation (b, d).

It follows from the obtained results that with annealing temperature increasing the Si(O) -78 eV content increases at the interface of both sample types, which evidences continuous oxidation of Si layer on the interface and thickness increasing of this oxidized layer. Herewith, on ALD samples the thickness of this SiOₓ layer at equal annealing temperatures is significantly lower than on Al₂O₃ specimens deposited by electron beam evaporation.

For more detailed profile analysis of the obtained layers and their evolution upon rapid thermal annealing the ion fragmentation was analyzed by time-of-flight secondary ion mass spectrometry. Figure 4 illustrates the distribution profiles of ion fragments of Al₂O₃ layers on Si substrate formed by ALD and electron beam evaporation techniques before and after thermal processing at 800°C and 1000°C.

As follows from the obtained results, upon Al₂O₃ film deposition by electron beam evaporation preliminary cleaning procedure was applied which can lead to increase amount of dangling bond imperfections on the substrate surface and substrate heating upon deposition, which highly increases the chemical activity of Si, thus, leading to Si surface layer oxidation upon interaction with high energy aluminum oxide particles. The obtained results are in good agreement with the results of Auger spectroscopy. On the other hand, in a samples formed by ALD it was possible to detect Si-O-Al bonds on the transient layer. Existence of such bonds can be attributed to possible chemical surface reactions occurring upon contact between SiO₂ and Al(CH₃)₃ couples [18]:

\[
\text{Si-OH} + \text{Al(CH₃)₃} \rightarrow \text{Si-O-Al(CH₃)₂} + \text{CH₄}
\]

\[
2 \text{Si-OH} + \text{Al(CH₃)₃} \rightarrow (\text{Si-O})₂=\text{Al(CH₃)₂} + 2\text{CH₄}
\]

\[
(\text{Si-O})₂ + \text{Al(CH₃)₃} \rightarrow \text{Si-O-Al(CH₃)₂} + \text{Si-CH₃}
\]
which, probably, evidences incomplete decomposition of TMA on substrate surface upon interaction with water at initial stages of deposition.

Distributions of CH groups in both cases are nearly identical. The SiO₂ signal in ALD is, most probably, related with natural oxide of substrate and is insignificant. The absence of the SiO₂ signal in ALD Al₂O₃ in profile distributions obtained by Auger spectroscopy is related with higher sensitivity of ToF-SIMS. Similarly, there is no carbon signal obtained by Auger spectroscopy in profile distributions of structures formed by electron beam evaporation.

Figure 4. Distribution profiles of ion fragments of Al₂O₃ layers deposited by ALD (a, c, e) and electron beam evaporation (b, d, f) before (a, b) and after thermal processing at 800°C (c, d) and 1000°C (e, f).
Upon rapid thermal annealing at 800°C CH groups in a sample obtained by ALD are localized, which is a consequence of increased roughness of the deposited layer in comparison with non-annealed specimen, and CH groups in a sample obtained by electron beam evaporation are still uniformly distributed across interface. Increasing of the silicon oxide layer thickness at the interface upon thermal oxidation is also obvious. Upon further annealing temperature increasing up to 1000°C CH groups at the interface of sample obtained by ALD are almost completely absent, and the silicon dioxide signal propagates from the transient layer into the depth of the substrate, which is most probably related with peculiar features of ToF-SIMS analysis method of the samples with highly rough surface (Fig. 2e). In samples formed by electron beam evaporation CH groups remain distribution across the analyzed surface on the transient layer even upon annealing at 1000°C with uniform. Continuous silicon oxide layer thickness increasing is also observed in both sample types.

CONCLUSIONS

Therefore, in current work peculiar features of such passivating layers deposition procedures for micro- and functional electronics as atomic layer deposition and electron beam evaporation has been studied in details. These procedures has been compared upon deposition of aluminum oxide thin passivating layers on monocrystalline Si substrates before and after processing of samples upon rapid thermal annealing (RTA) in Ar environment at 800°C and 1000°C. Auger spectroscopy and time-of-flight secondary ion mass spectrometry have been applied for profile analysis of the obtained samples. The obtained results demonstrate that the surface morphology of initial samples is smooth. However, upon samples thermal processing the surface morphology varies and becomes rougher. It is demonstrated that upon Al₂O₃ deposition by electron beam evaporation Si substrate already starts to oxidize. Such feature can put additional contribution to optical and electrophysical properties of the functional structures. In addition, existence of CH groups at Al₂O₃-Si interface has been detected in both cases. As a consequence of thermal processing Si is oxidized and SiOₓ thickness under Al₂O₃ layer increases, however, when ALD is used for deposition the oxidized silicon thickness is lower by more than 1.5 times comparing to the sample obtained by electron beam evaporation technique. In addition, upon analysis of obtained samples by ToF-SIMS the signal of CH groups disappear in the samples with aluminum oxide layer deposited by ALD after annealing at 1000°C contrary to EBE where CH groups still existed in Al₂O₃/Si transient layer. Such impurities can make additional uncontrolled contribution to the properties of produced layers. Hence, it is demonstrated that ALD is one of the most advanced deposition procedures of passivating and antireflection functional layers in photovoltaics.

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REFERENCES