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In-situ diagnostics of PECVD AlO_x deposition by optical emission spectroscopy

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ABSTRACT

Plasma enhanced chemical vapor deposition (PECVD) is ubiquitously used in the crystalline silicon photovoltaics industry to deposit surface passivation and anti-reflection coatings. Aluminum oxide deposited by PECVD is becoming an increasingly common rear surface passivation layer, due to the growing market share of solar cells with partial rear contacts, such as the passivated emitter and rear solar cell. In this study, we use *in-situ* monitoring to investigate the correlation between the PECVD plasma properties and the resulting aluminum oxide film properties. Although no linear correlation between the density of the constituent radicals (aluminum, oxygen, and hydrogen) in the plasma and the surface passivation quality was observed, we did identify optimum processing conditions for a high quality surface passivation layer using *in-situ* plasma monitoring. This study also highlights the limited knowledge that currently exists within the photovoltaic community regarding plasma characterization and its impact on device performance.

1. Introduction

Aluminum oxide (AlO_x) has become increasingly important in photovoltaics (PV) manufacturing due to its outstanding capability to passivate the surfaces of silicon (Si) solar cells, in particular for *p*-type and p^+ surfaces [1–6]. The material provides both excellent field effect passivation - due to a high density of negative charge within the film - and chemical passivation, due to its high concentration of hydrogen atoms [1–6].

Plasma-enhanced chemical vapor deposition (PECVD), which is widely used for the formation of dielectric films in both the nano-electronics [7–25] and PV manufacturing industries [4,6,26–31], is typically used to deposit AlO_x layers. Optimization of the deposition process is a key requirement to ensure optimized device performance. Common characterization methods used in the PV community include excess carrier lifetime measurements to assess the surface passivation quality of the obtained film [32–40] and Fourier transform infrared spectroscopy (FTIR) to determine the chemical bonding configuration of the deposited film [1,29,41–47].

However, these characterization methods can be used only after the deposition process, in separate systems. Development of *in-situ* monitoring methods can be valuable since process information and possible errors can be detected in real time during manufacturing. Optical emission spectroscopy (OES) is one of the most widely used methods for *in-situ* process monitoring in the nano-electronics industry [7–21,23–25]. However, it is not commonly used in the PV industry [48,49]. In this study, an OES-based method to monitor PECVD AlO_x is investigated; we then try to correlate the detected radicals with the chemical properties of the film and interface passivation quality.

As critical process parameters, the gas flow rate ratio (GFRR) between nitrous oxide (N_2O) and tri-methyl aluminum (TMA), the deposition pressure, and the deposition temperature were varied. These parameters are known to have a major impact on the film properties [28,50,51]. Total gas flow rate and microwave power are also important parameters; however, they were fixed at 900 sccm and 1500 W (32% duty cycle) in this study, to allow for a detailed study of the other three parameters. The density of aluminum (Al*), oxygen (O*), and hydrogen (H_α* and H_β*) radicals in the plasma were monitored by spectrophotometry as the intensity of the emitted light from the electronic transitions. H_α* and H_β* are spectral lines in the Balmer series which are detected when a hydrogen electron falls from the third (H_α*) and fourth (H_β*) lowest energy levels to the second lowest energy level. The impact of these parameters on the density of different radicals is analyzed using a statistical software package (STATISTICA [52,53]).

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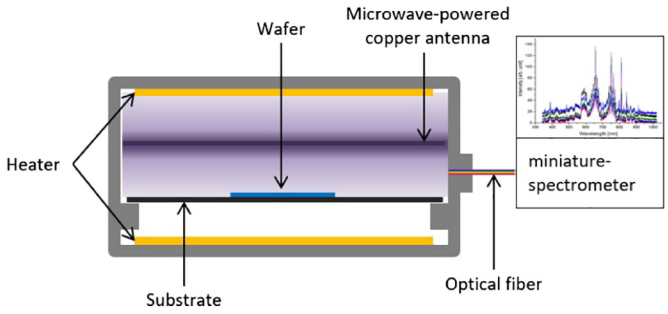

Fig. 1. Schematic diagram of OES set-up and the deposition system.

Although no strong correlation between the density of the forming radicals (Al* and O*) in the plasma and the surface passivation quality has been noted, we have determined the PECVD condition to achieve an optimum surface passivation layer. However, this study highlights the limited knowledge that currently exists within the PV community regarding plasma characterization and the relationship between the plasma species and surface recombination behavior.

2. Experimental methods

The OES was installed in an industrial PECVD system (MAiA, Meyer Burger). The schematic diagram of the modified system is shown in Fig. 1. Light emission from an electronic transition of the radicals in the microwave plasma is transferred by an optical fiber, which is mounted at view-port of the process chamber. The transferred light is analyzed by a miniature spectrometer (Ocean Optics USB 2000+) with a detectable wavelength range of 340 nm to 1020 nm. The density of the plasma radical is represented as the magnitude of the associated emission peak. Fig. 2 shows the peak information of the OES signal during a typical deposition process. The Al*, H_α*, H_β*, and O* related peaks are detected at the wavelengths 391.9 nm, 656.6 nm, 486.9 nm, and 777.8 nm, respectively (Table 2) [24,54].

Two groups of wafers were used in this study. The first group consists of 60 *p*-type, Czochralski (Cz), random-upright-pyramid textured wafers (resistivity of ~1.8 Ω·cm, thickness of 190 ± 10 μm and size of 45 × 45 mm^2). The second group consists of 15 2″ double-side-polished (DSP) *p*-type Cz wafers (resistivity 10 Ω·cm and thickness 175 ± 10 μm). The first group (Cz wafers) were used for electrical property measurements (excess carrier lifetime), while the second group (DSP wafers) was used for chemical property measurements (FTIR). The wafers went through an RCA (Radio Corporation of America) clean [55] and hydrofluoric acid (HF) dip before AlO_x and silicon nitride (SiN_x: serves as a capping layer) depositions.

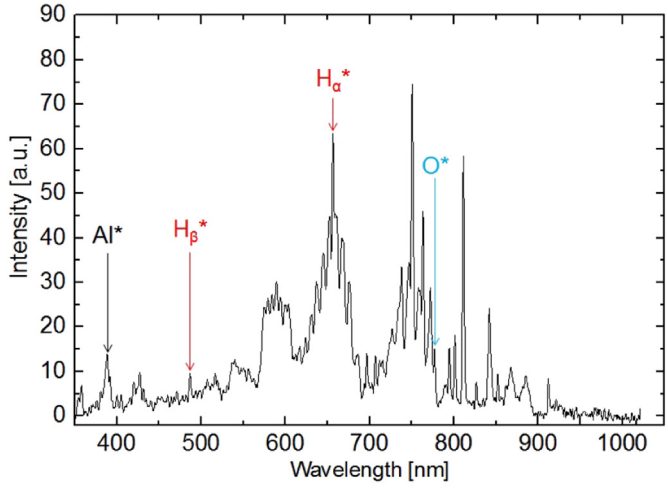

Fig. 2. A representative example of a OES signal as a function of wavelength; the peaks of Al*, H_β*, H_α*, and O* are marked.

Table 1
All the values of three process parameters designed by STATISTICA.

Run number	Temperature [°C]	Pressure [mbar]	Gas ratio [N_2O/TMA]
1	350	0.095	5.0
2	350	0.080	7.5
3	350	0.110	7.5
4	350	0.095	10.0
5	375	0.080	5.0
6	375	0.110	5.0
7	375	0.095	7.5
8	375	0.095	7.5
9	375	0.095	7.5
10	375	0.080	10.0
11	375	0.110	10.0
12	400	0.095	5.0
13	400	0.080	7.5
14	400	0.110	7.5
15	400	0.095	10.0

For AlO_x deposition, N_2O and TMA were used as process gases with argon (Ar) as a carrier gas for TMA. Silane (SiH_4) and ammonia (NH_3) were used for the SiN_x deposition. The same SiN_x capping layer was used for all the Cz samples. Although the SiN_x was not deposited onto the DSP wafers, they received the same thermal treatment by passing them through the PECVD system with the plasma sources switched off, while keeping the same setting for the heaters and for the transport. Thickness of the AlO_x layers was targeted at 25 nm to avoid thickness dependence of the surface passivation performance. In this work, FTIR and lifetime results are limited to as-deposited samples to avoid any possible modification of the film property by the subsequent thermal process.

With regard to characterization of the resulting film, effective surface recombination velocity (S_{eff}) was extracted from photoconductance-based effective lifetime measurements (using WCT-120 from Sinton Instruments). For extracting S_{eff}, we used equation below,

$$S_{eff} = \frac{W}{2}\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{int}}\right) \quad (1)$$

where τ_{int} is the intrinsic (Auger and radiative) lifetime. Here we assume that $\tau_{SRH}{}^{-1}$ (infinite bulk lifetime) equals zero since the quality of the bulk is low due to inherent B-O and iron in Cz wafers. In this case, the calculated S_{eff} is at its upper limit.

Each wafer was measured in quasi-steady-state mode [56]. An FTIR spectrometer (Nicolet 5700 from Thermo) was used to measure the infra-red absorption by various chemical bonds in the AlO_x films (Table 3).

Analysis of the data was done using STATISTICA. The experiment was designed as a Box-Behnken (3 factors/1 block/15 runs with 3 levels) with the three independent factors chosen to be GFRR of N_2O to TMA,

Table 2
Wavelength values for the selected species detected by OES (N_2O/Ar/TMA PECVD system).

Species	O* line	H_α* line	H_β* line	Ar* line	Al* line
Wavelength (nm)	777.8	656.6	486.9	420.8	391.9