Detection of electronic defects in semiconductor thin-films during plasma processing

半導体プラズマプロセス中の薄膜材料の欠陥検出

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In semiconductor device fabrication, a variety of thin-film materials are deposited and etched away by means of plasma processing technology. The device performance is often limited by electronic defects, which are generated in the film during plasma processing. So, it is necessary to reduce these defects by precisely controlling the plasma processing, based on the knowledge of the defect generation and annihilation kinetics. In this study, we have developed an unique technique for detecting the electronic defects by measuring the photocurrent(*) in the film under illumination of light at two different wavelengths. Using this in-situ and real-time technique, the defect generation and annihilation are successively monitored during plasma processing. The defect monitoring is useful for the development of advanced plasma processing, that is required for state-of-the-art semiconductor devices. Although the developed technique is demonstrated under the plasma deposition process of amorphous silicon films for solar cell applications, it can be applied to other semiconductor plasma processing, including etching and surface treatments.

* Photocurrent is the electronic current in the semiconductor materials, excited by illumination of light. The illumination of light generates free electron-hole pairs in semiconductors.

半導体デバイスの作製には，様々な薄膜材料の成膜（デポジション）と加工（エッチング）がプラズマプロセス技術を用いて繰り返し行われる。デバイスの性能は，プロセス中に生じる薄膜材料の欠陥（electronic defects）によって制限されるが，これまでその欠陥をプロセス中に検出する技術がなく，欠陥の発生と修復のメカニズムは十分に理解されていなかった。そこで、本研究では，薄膜材料に二種類の異なる波長の光を照射し光電流(*)を計測することで，欠陥をその場でリアルタイムに検出する技術を開発した。本技術を用いることで，プロセス中に欠陥をモニタリングすることが可能になり，また，欠陥のモニタリングを通して，デバイスの高品質化や歩留まり向上を効果的に進めることが可能になる。本稿では，太陽電池向けアモルファスシリコンの成膜プロセスを対象に本技術を紹介するが，エッチングや表面処理等の他の半導体プラズマプロセスにも適用可能である。

＊物質に光を当てたとき，その光を吸収して光電子と呼ばれる自由電子を生じる。この光電子の運動による電流を光電流という。

Introduction

Semiconductor devices such as logic circuit, memory and optoelectronic devices play important roles in IoT (Internet of things) and AI (artificial intelligence)-based next-generation global society. The semiconductor devices usually consist of nanostructured p-n junctions, which are fabricated by means of plasma processing. In plasma processing, a variety of semiconductor and/or insulating thin-films are deposited and etched away in many times. The

performances of these devices are governed by the optoelectronic property of the deposited films,[1] which are strongly influenced by each processing step.[2] Thus, one need to precisely control the plasma processing in order to obtain the designed optoelectronic property of the films. However, the details of the plasma and gas-phase parameters as well as the optoelectronic property of the films are not fully understood during plasma processing. So, further development of advanced plasma processing has been limited.

In this study, we have developed two kinds of techniques to understand the whole pictures of the plasma processing and precisely control it. (i) One is a technique for comprehensively measuring the plasma and gas-phase parameters.[3] (ii) The other is a technique for measuring the optoelectronic property of the films during plasma processing.[4] Combining these two techniques opens the door for developing the advanced plasma processing, which is required for high-performance device fabrication for the next-generation IoT and AI.

The developed techniques were demonstrated under the plasma deposition process for hydrogenated amorphous silicon (a-Si:H). This material is widely used as photovoltaic materials, passivation layers, and thin-film transistors. The a-Si:H is also expected to be a key material in flexible IoT devices. In the following sections, we describe the methodology and apparatus, followed by the measurement results.

Comprehensive measurement of the plasma and gas-phase parameters

A schematic view of plasma diagnostics is shown in Figure 1.[5] The deposition plasma was diagnosed with the following tools: Langmuir probe (LP), optical emission spectroscopy (OES), mass spectrometry (MS), absorption spectroscopy, and laser light scattering (LLS). The plasma parameters, i.e., the electron temperature and density, were measured with LP, while the gas composition and ion species were measured with MS. The generation of radicals such as H atoms was monitored by OES. The particulates (clusters and nanoparticles) generated in gas phase were detected by LLS. Using these methods simultaneously, we can comprehensively collect the plasma and gas-phase parameters in a single batch of discharge, and thus we can study the plasma-related gas-phase physics and chemistry.

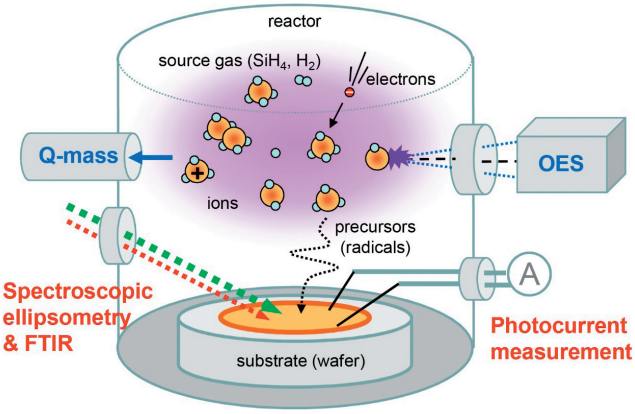

Figure 1 Schematic view of experimental setup. The setup consists of two parts: plasma diagnostics (upper part) and in-situ material characterization (lower part). A plasma is diagnosed with Langmuir probe (LP), optical emission spectroscopy (OES), mass spectrometry (MS), absorption spectroscopy, and laser light scattering (LLS).[5] The optoelectronic property of a growing semiconductor film is determined from spectroscopic ellipsometry (SE) and in-situ photocurrent measurement, based on an optical pump-probe technique[4]

An example of measurement results on the plasma and gas-phase parameters as a function of the discharge time, t, is shown in Figure 2.[3] The deposition plasma was generated by capacitively coupled 60 MHz discharge of hydrogen (H_2) and silane (SiH_4) gas mixture. The discharge conditions are following: a gas pressure of 9.7 Torr, a H_2 gas flow of 98 sccm, a SiH_4 gas flow of 2 sccm, a discharge power of 0.78 W/cm^2. The discharge was maintained for t = 600 s. The data were collected with an acquisition unit at every 10 ms.

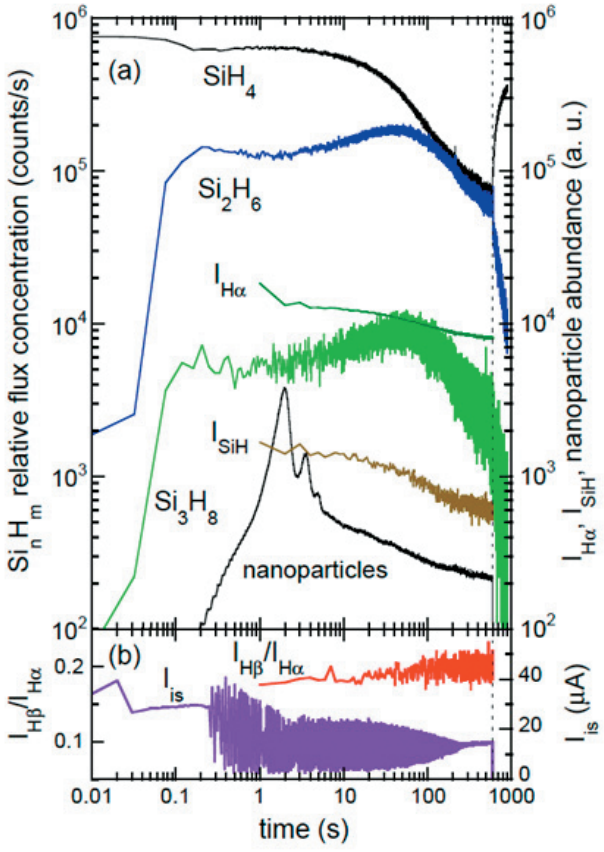

Figure 2 Time evolutions of plasma and gas-phase parameters.[3] (a) Relative densities of SiH_4, Si_2H_6 and Si_3H_8 measured with MS, H_α and SiH emissions ($I_{H\alpha}$ and I_{SiH}) from OES, and particulate amount measured by LLS. (b) Plasma-related parameters such as high-energy electrons, monitored by $I_{H\beta}/I_{H\alpha}$ and ion saturation current, I_{is}.

As apparent, the plasma and gas-phase parameters are highly time-dependent in a wide range of time scales from 10 ms to 100 s. The initial and steady-state plasmas are different each other even though the discharge conditions are kept constant. Such a large variation in a deposition plasma results from various gas-phase reactions and diffusion. Within t ≈ 100 ms, the feedstock gas of SiH_4 is dissociated, and disilane (Si_2H_6) and trisilane (Si_3H_8) molecules are generated via polymerization reactions. After a while (t ≈ 1 s), a large amount of particulates are formed, inducing an instability in plasma, indicated by the fluctuation in the ion current. In a time scale of t ≈ 10 s to 100 s, polymerized species such as Si_2H_6 and Si_3H_8 are build up in the reactor. Later (t ≈ 100 s and more), the source gas of SiH_4 is strongly depleted due to a limited feedstock supply.

From the viewpoint of the film formation, such time-dependent gas-phase composition and plasma parameters are unfavorable, because they may cause the unexpected inhomogeneity of the optoelectronic property of the film. The measurement results suggest that the short-term initial transient should be minimized to control the interface property and initial growth. The long-term transient should be suppressed to control the bulk property and vertical homogeneity.[4]

In-situ measurement of the optoelectronic property of semiconductor thin-films

The measurement setup for the optoelectronic property of the growing films is shown in the lower part of Figure 1. The optical property such as the band gap, E_g, the refractive index, n, and the extinction coefficient, k, was determined from spectroscopic ellipsometry (SE). The electronic property such as carrier transport and electronic defect states was characterized via the photocurrent measurement,[4] based on an optical pump-probe technique.[6]

The methodology for defect monitoring is following. We measured two kind of electrical currents in the film: the photocurrent under the pump light and the trap current, i.e., an increase of the photocurrent, under the probe light. The pump-induced photocurrent is inversely proportional to the defect density, and therefore a change of the photocurrent reflects the generation or annihilation of the defects. On the other hand, the probe-induced trap current gives the trapped carrier density (n_t), proportional to the defect density.[4, 6]

$$n_t = \frac{\sigma_v}{\sigma_t} \cdot \frac{\Gamma_{pump}}{\Gamma_{probe}} \cdot \frac{I_t}{I_p} \cdot n_v, \quad \cdots\cdots (1)$$

where, Γ_{pump} and Γ_{probe} are the photon fluxes of the pump and probe light, respectively. σ_v and σ_t are photo-absorption cross sections for the valence and trapped electrons. n_v is the valence electron density. In this study, a visible laser (520 nm wavelength and 1 mW output) was used for the pump while a near-infrared laser (1340 nm wavelength and 500 mW output) was used for the probe.

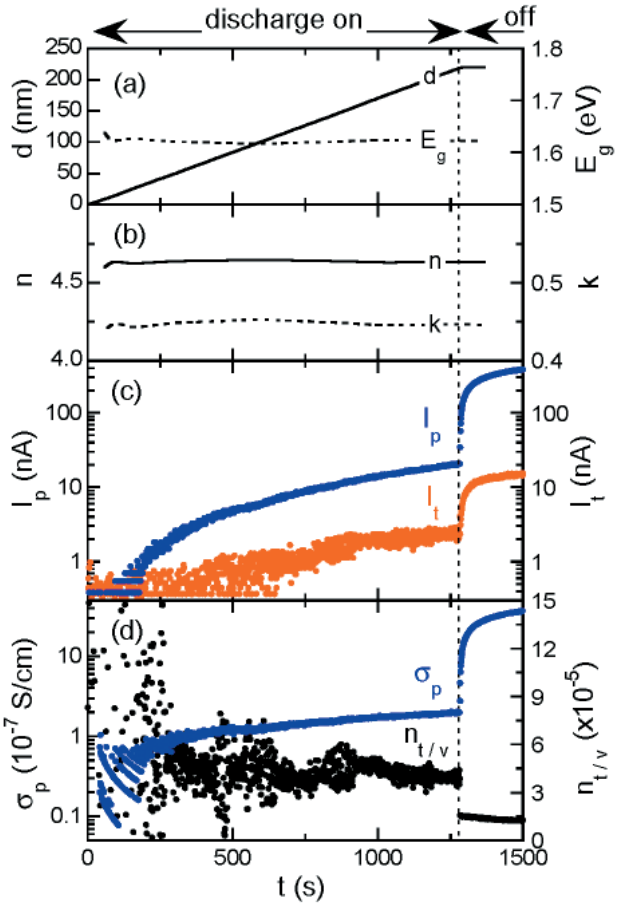

Figure 3 In-situ measurements of optoelectronic property of a-Si:H films during plasma deposition process.[4] The discharge was terminated at t = 1270 s, at which the post-deposition annealing was initiated. (a) Film thickness, d, and the energy bandgap, E_g, (b) the refractive index, n, and the extinction coefficient, k, obtained from SE. (c) Photocurrent, I_p, excited by the pump and trap current, I_t, excited by the probe. (d) Photoconductivity, s_p, and normalized trapped carrier density, $n_{t/v}$, calculated by Equation 1.

Figure 3 shows measurement results of the optoelectronic property of an a-Si:H film during the growth.[4] The discharge conditions are following: a gas pressure of 0.3 Torr, H_2 gas flow of 53 sccm, SiH_4 gas flow of 7 sccm, a discharge power of 0.03 W/cm^2. The growth temperature was 200 °C. The discharge was maintained for t = 1270 s. As in Figure 3a, the film thickness, d, was increased linearly with the deposition time (growth rate ≈ 0.17 nm/s). The optical property such as E_g, n, and k was nearly constant during the growth, which indicated a homogeneous film growth in terms of the optical property (Figure 3b).

On the contrary, the electronic property is highly

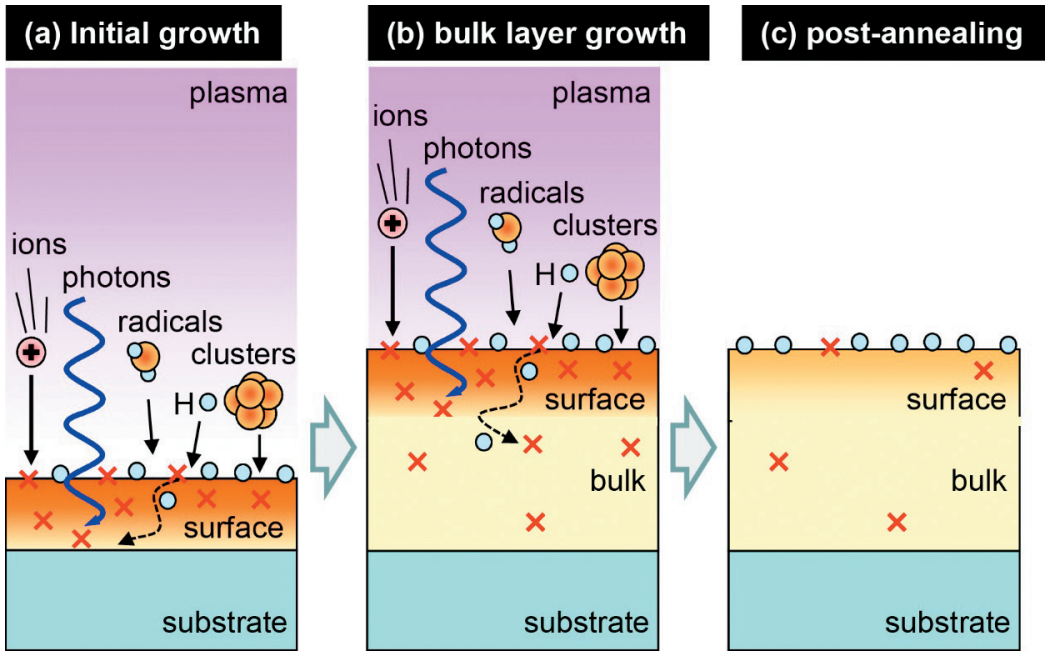

Figure 4 Film structure and defect distribution during plasma deposition processing. (a) Ultrathin film at the initial growth. The film has a large amount of defects, which restricts the carrier transport. (b) Thick-film growth during deposition process. The defect-rich surface layer is formed near the surface, due to energetic particles from the plasma. Underneath, the bulk layer is grown. (c) Post-deposition annealing. The defects generated during the plasma deposition are effectively annihilated by the thermal annealing.

dependent on the deposition time, i.e., the film thickness, indicated by the large variation in the photocurrent shown in Figure 3c. Initially, the photocurrent in an a-Si:H ultrathin film (below d ≈ 20 nm) was not observed. The photocurrent was observed once the thickness approaches to d ≈ 20 nm, and gradually increased with the deposition time, i.e., the film thickness. The trap current behaved a tendency similar to that of the photocurrent. With this data and Equation 1, the trapped carrier density was estimated to be ≈ 10^{18} cm^{-3}. The photoconductivity, σ_p, calculated from the photocurrent and film thickness, approached to the constant value once the thickness exceeded d ≈ 100 nm (Figure 3d), which was expected and revealing the bulk property.

Interestingly, the photocurrent was significantly increased after the deposition (t > 1270 s), i.e., during the post-deposition annealing. It means that the electronic defects generated during the plasma process are efficiently annihilated by the post-annealing. Such a defect annihilation process was successively monitored via the in-situ photocurrent measurement, which has not been fully studied so far.

The measurements suggest the following new aspects of the film structure and defect kinetics (see Figure 4). (i) At the initial growth, a large amount of defects are generated in an ultrathin film of thickness below d ≈ 20 nm. The carrier transport is highly limited, and thus the photocurrent is not observed. (ii) During the thick film growth (d > 20 nm), the defect-rich surface layer is formed. Underneath it, the bulk layer is grown, as the film becomes thicker with the deposition time. (iii) The defects generated during the plasma deposition process are annihilated effectively by the post-deposition annealing.

Summary

We have developed two kinds of unique techniques in order to understand the whole pictures of the plasma processing and precisely control it. Firstly, we developed a technique for comprehensively measuring the plasma and gas-phase parameters. This technique yields a set of data for studying the plasma-related gas-phase physics and chemistry. Secondly, we developed a technique for measuring the optoelectronic property of the films during plasma processing. In particular, in-situ photocurrent measurement is extremely useful for monitoring the defect generation or annihilation. Combining these two techniques opens the door for developing the advanced plasma processing, which is required for high-performance semiconductor device fabrication for the next-generation IoT and AI.

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