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Deposition of microcrystalline silicon in electron-cyclotron resonance discharge (24 GHz) plasma from silicon tetrafluoride precursor

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ABSTRACT

Deposition of Si films is done in a high power 24 GHz gyrotron-based electron-cyclotron resonance plasma enhanced chemical vapour deposition setup. The possibility of high-rate (2.5 nm/s) deposition of thin silicon films from $SiF_4 + H_2$ plasmas in an electron-cyclotron resonance reactor with gyrotron microwave plasma source at the frequency of 24 GHz is demonstrated. The analysis with spectroscopic ellipsometry and Raman scattering shows that films have large crystalline fraction (75%) with an average size of silicon grains of 3 nm. The use of gyrotron with high microwave power opens up the possibility to make depositions from high density plasmas at pressures of tens of pascals, which results in high deposition rates (tens nm/s).

1. Introduction

Microcrystalline silicon is a promising material for various applications, especially in the field of thin film solar cells and thin film transistors. The modern trend in thin film photovoltaics is the use of cells based on micro-(μc-Si:H) or nanocrystalline (nc-Si:H) silicon in combination with amorphous silicon (a-Si:H) in tandem (so-called “micromorph”) or triple junction solar cells (Kaneka Co., Sharp Co., Unisolar Co. [1]) to achieve high stable efficiencies. The top a-Si:H based solar cell absorbs the visible light and leaves the infrared part of the spectrum for the bottom μc-Si:H based solar cell. Record stabilized efficiencies in triple junction solar cells have reached 12.5% at EPFL [2] and 13.4% has been achieved by LG [3]. Semiconductor industry is also investigating the potential of p-doped μc-Si:H, especially in thin-film transistor (TFT) production, in order to realize complementary metal–oxide–semiconductor circuitry with TFT transistors. Moreover, silicon nanocrystals can be used as photosensitizers in photophysics and photochemistry, biology, in medicine (photodynamic cancer therapy) etc.

One of the most pressing challenges in reducing the production costs of solar cell is the deposition of high quality μc-Si:H films at high rate (up to several nm/s) for intrinsic layer absorber. Numerous efforts are aiming now to achieve such high deposition rates, most notably through utilization of high-density plasmas. In radiofrequency (RF) capacitively coupled plasma (CCP) discharges this typically achieved with increase of RF power, but that increases in the sheath voltage and above certain value radiation damage from ions render films highly defective. One of the approaches is to use electron cyclotron resonance (ECR) discharge for plasma enhanced chemical vapour deposition (PECVD) of silicon from gas precursors. The important feature of ECR discharge plasmas is the possibility to deposit layers at very high rate due to their high electron density resulting in high dissociation efficiency. The advantage of ECR discharges in comparison with inductively coupled plasma RF discharges is in the absence of any dielectric materials in the discharge area, like the absence of quartz chamber walls, required with the use of external coils. The area of ECR discharge is determined by location of the zones of resonant ECR absorption of microwave radiation and can be arranged to be far away from the walls. Besides, the ion energy in ECR plasmas is significantly lower than in CCP discharges, for example, and that minimizes sputtering of the walls of the reactor as well as radiation damage on the growing layer. The reactor is placed in the external magnetic field, which also restricts the ion motion in the

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direction towards the walls. So ECR discharges are ideally suited for high-rate production of high-purity materials, in particular, silicon thin films, however scale-up, achieved in RF-CCP systems, remains very challenging problem.

Deposition of silicon films in ECR plasmas is traditionally done with 2.45 GHz microwave plasma in 875 G resonant magnetic field at low pressure (0.1 Pa range). First amorphous silicon films were deposited from SiH_4/H_2 mixtures by Shing et al. [4] in 1989. Then numerous experiments were aimed at the ECR deposition of microcrystalline silicon films from different silane mixtures [5,6]. In these works the deposition rate of silicon films didn't exceed 1 nm/s in the pressure range 0.1–2 Pa. The deposition of microcrystalline silicon films in ECR discharges was investigated later [7–13]. It was also reported [14] that the deposition of μc-Si:H from SiH_4 in matrix distributed ECR plasma reactor can achieve the rate of up to 2.8 nm/s. But solar cell manufacturing demands even higher deposition rates and since critical electron density scales with microwave frequency, we may search for microwave generators for plasma sources along that direction. One such higher frequency microwave generator is a gyrotron. Gyrotrons are used for many industrial and high technology heating applications. For example, gyrotrons are used in nuclear fusion research experiments to heat plasmas, and also in manufacturing industry as a rapid heating tool in processing of glass, composites, and ceramics, as well as for annealing processes.

In our previous study [15] the technological gyrotron with frequency 24 GHz and power level up to 5 kW was applied for the decomposition of silicon tetrafluoride. That allowed us to perform the deposition of silicon at high microwave power and to demonstrate a density of absorbed power in the plasma as high as 100 W/cm^3. The use of microwave radiation of gyrotron with such a high frequency promises to increase significantly the plasma density in a PECVD reactor, and as the result, it is expected to increase the rate and efficiency of dissociation reactions. The approach for producing high-purity silicon with isotopic enrichment of ^{28}Si isotope in plasma of ECR discharge, sustained by microwave radiation of gyrotron with the frequency of 24 GHz has been demonstrated recently [16]. Moreover thick microcrystalline diamond films were grown on silicon substrates with 60–90 mm in diameter in the PECVD reactor based on 10 kW gyrotron operating at a frequency of 30 GHz [17,18].

In this article we present the results of experiments on the growth of thin μc-Si:H layers from $SiF_4 + H_2$ plasma in ECR reactor with gyrotron microwave plasma source at a frequency of 24 GHz. The silicon tetrafluoride was chosen as a precursor because it is neither combustible nor explosive (unlike silane), and in the case of low humidity is very stable. SiF_4 has the highest mass fraction (27%) of silicon in comparison with other silicon halogenides. The material source base of silicon tetrafluoride is essentially unlimited because it is the waste product of mineral processing.

2. Experimental setup

We performed our studies using a gas discharge sustained by the electromagnetic radiation of a gyrotron in the magnetic field under electron cyclotron resonance conditions. A sketch of the experimental deposition reactor is shown in Fig. 1.

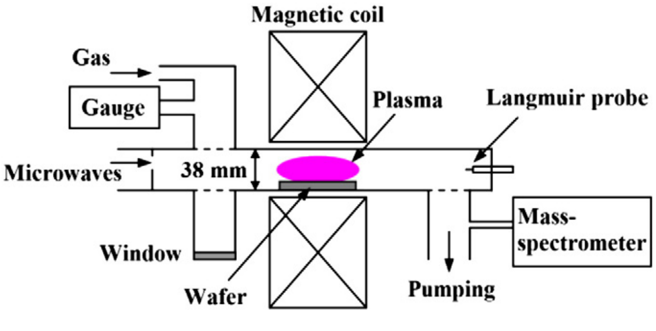

Fig. 1. Sketch of the experimental system.

Continuous-wave radiation (TE11 mode) of a gyrotron with a frequency of 24 GHz propagates through the plasma-coupling device into the centre of the discharge chamber. The construction of plasma-coupling device provides the transmission of more than 90% of microwave power, also protecting the gyrotron window from plasma fluxes and reflected radiation from plasma. The microwave power can be varied from 0.1 to 5 kW. The details of experimental PECVD system can be found in [15].

The discharge chamber consists of a cylindrical stainless tube (38 mm in diameter with a length of 60 cm) with the flattened bottom inside the deposition area. In the central section of the tube, two ports are situated: from one side a quartz window for optical diagnostics and from the opposite side a port which is used for gas injection and pressure monitoring. The working gas mixture of hydrogen (H_2) and silicon tetrafluoride (SiF_4) is introduced into the discharge chamber through the injection port. The flow of the gases is controlled by mass-flow controllers with a range of 1 to 500 sccm. The pressure of working gas in the chamber is measured by a baratron. The gas is evacuated from the chamber through the pumping port, located at the end of the tube, either by scroll pump or by turbomolecular pump. The operating pressure range is 5–500 Pa in the case of using a scroll pump, and 0.001–1 Pa for turbomolecular pump. The discharge chamber is partly placed in magnetic field, produced by magnetic coil of Bitter type with water cooling. The maximum magnetic field strength is about 1 T, reached with a current of 750 A. Deposition time was always kept at four minutes.

After the gas breakdown the plasma is resonantly sustained at the fundamental gyrofrequency. The ECR absorption region occupies the position near the centre of the magnetic coil and corresponds to the magnetic field strength of 0.86 T.

Silicon was deposited on glass substrates (Corning 1737 2.5 × 2.5 cm, 1 mm thick), placed on the flat bottom of vacuum chamber. The bottom side of the chamber was cooled externally with water at room temperature (~20 ˚C). The substrate was placed in the region, where the ECR conditions for 24 GHz are fulfilled (ECR-zone).

The Raman spectrum of the sample was acquired under excitation by blue light laser at a wavelength of 473 nm at room temperature using LabRam Raman spectrometer coupled with confocal microscope. The power of laser beam was controlled in a way not to affect (crystallize) the sample.

Secondary ion mass spectrometry (SIMS) measurements were used to qualitatively determine certain impurities in the silicon films. The elemental composition was analysed using SIMS with a TOF-SIMS-5 instrument (IONTOF). For the in-depth analysis, we have used an ion gun of O^{2+} ions with an energy of 2 keV, a beam current of 500 nA, and a beam diameter of 100 μm or Cs + ions (2 keV, 300 nA, and 50 μm). These beams were scanned in the 120 × 120 μm raster pattern.

A spectroscopic ellipsometer (UVISEL) was used to determine the optical properties of the films. The spectra were taken between 1.5 and 4.8 eV with a step of 0.01 eV. Data were fitted in the frame of classical for microcrystalline silicon 3-layer model (seed layer, main layer and roughness) taking into account the incoherent reflection from the back side of the Corning glass. The thickness of each layer and its composition were obtained with DeltaPsi 2 software.

3. Experimental results and discussion

Here we present the results of experiments in which silicon was deposited from SiF_4 on a Corning glass substrate. In all experiments the power of microwave emission of gyrotron was 250 W during the deposition time of four minutes. The SiF_4 and H_2 flows were 12 sccm and 18 sccm respectively and the working pressure was 11 Pa.

An evidence of the presence of nanocrystals in the deposited layers was obtained from the analysis of the Raman spectra. Fig. 2 shows the