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DEPOSITION OF NANOCRYSTALLINE SILICON FILMS INTO LOW FREQUENCY INDUCTION RF DISCHARGE

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Results of experiments on obtaining nanocrystalline silicon films with the method of stimulated plasma-enhanced chemical vapor deposition (PECVD) into low frequency induction RF discharge (880 kHz) allowed in silicon tetrachloride diluted with hydrogen are presented. High rate value, as 2.41 nm/s, of silicon film deposition was achieved. X-ray diffraction phase-shift analysis was pursued, the value of unit spacing of crystalline lattice was determined and nanocrystalline silicon film structure was studied.

INTRODUCTION

At present thin films of nanocrystalline silicon are widely used both in microelectronics and for manufacturing photoelectric transducers of solar cells [1-3].

Electrophysical properties of nanocrystalline silicon films obtained are significantly depends on grain structure, type and size, which are determined by techniques of processing and anong them are thermal decomposition (CVD), hydrogen reduction and plasma-enhanced chemical vapor deposition (PECVD) of siliceous compounds such as trichlorosilane ($SiHCl_3$), monosilane (SiH_4) and silicon tetrachloride ($SiCl_4$).

Processes of thermal decomposition and hydrogen reduction are power consuming and inefficient.

Therefore, at present in order to obtain silicon films methods of plasma chemical hydrogen reduction of silicon compounds using capacitive and induction RF discharges working mainly in high-frequency range ($V_{ex} \geq 13.5$ MHz) or in microwave range.

Using capacitive RF plasma high rates (0.8…1.4 nm/s) of silicon film growth were achieved [4].

However significant disadvantage of using capacitive discharges is contamination of silicon films by resultant products of reactions of plasma subversive gases (gaseous halogenides of Si, Cl and HCl) with electrodes.

The mentioned disadvantage is absent in plasma of induction RF discharge since a RF inductor establishing plasma is situated outside of discharge chamber.

Plasma chemical reactions of hydrogen reduction are pursued under equilibrium conditions and high pressure (up to air one), and under non-equilibrium conditions at low pressure.

In low temperature non-equilibrium plasma electronic temperature and vibrational-band temperature of molecules of vapour-gas mixture exceed gas translational temperature, which allows to accerate direct processes of end product obtaining and slow down backward reactions [5-11].

The aim of this study was to obtain nanocrystalline silicon films by hydrogen reduction of silicon tetrachloride ($SiCl_4$) into low temperature non-equilibrium hydrogen plasma at frequency of exciting electromagnetic field of 880 kHz.

MATERIALS AND METHODS

Studies on silicon nanocrystalline film deposition were carried out on an experimental assembly consisted of an evacuated vessel, a pumping unit, a reagent supply system and a RF discharge initiation system (Fig. 1).

The evacuated vessel consisted of a tube of quartz glass 150 mm in diameter and 600 mm in height (2) installed vertically between two antechambers (1) of stainless steel.

The quartz tube was cooled by air flow made by a ventilator (5) with capacity of 0.1 kW.

On the upper and lower antechambers inputs for reagent feed and outputs of evacuating systems as well as pressure control gauges were mounted.

The evacuating systems consisted of vacuum pump (6), nitrogen trap (7) and shutoff valves (12).

The reagent feeding system included the hydrogen cylinder (8), pressure reductor gear (9), hydrogen pressure control manometer (10), refrigerating trap (7), hydrogen flow meter (11), and container with silicon tetrachloride ($SiCl_4$) (15) placed on AXIS A6000 electronic scales (18) with measuring error of 0.1 g.

With the aim to stabilize silicon tetrachloride vapour pressure its container (15) was placed into the thermostat (14).

Gas flow rate control both in the evacuating system and the feeding system was performed with the aid of shutoff valves (12) and pressure regulating valves (13).

Pressure into the chamber was measured with the aid of a ВИТ-3 vacuum gauge (16) with measurement range between 20 and 10^{-5} pascal and a ВД-1 vacuum gauge with measurement range between 1.3 and 1330 Pa .

The system of RF discharge excitation consisted of an RF generator (19), an interface unit (20), a water-cooled inductor (3) and an electromagnetic radiation shield (4).

Frequency of 880 kHz used in the process of plasma-enhanced chemical reduction was obtained on the modernised ВЧИ-63/0.44 generator. When modernased its standard loop inductor of the load circuit was substituted for a multiple-turn one.

The generator was placed in continuous wave lasing by substituting an adjustable thyratron rectifier for a non-adjustable diode one. This substitution permitted to increase sufficiently reliability and stability in generator performance.

Generation rate was increased up to 880 kHz with the aid of change of capacitance in resonant/oscillator circuits of the generator. Stable performance of the generator under various magnitudes of output power was ensured by dividing matching and power adjustment circuits. Continuous adjustment of output power of the generator was carried out by a variable-ratio autotransformer set up on the input of power source. Also continuous trim in resonance of load and anode circuits was provided.

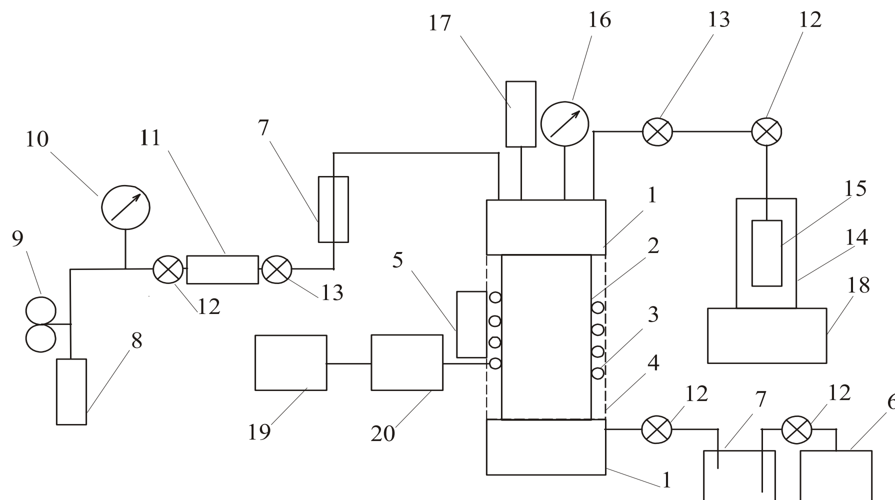

Fig. 1. The experimental assembly for obtaining silicon films into induction RF discharge:
1 – antechamber; 2 – quartz tube; 3 – inductor; 4 – protective case;
5 – ventilator; 6 – forepump; 7 – nitrogen trap; 8 – hydrogen cylinder;
9 – reduction gear; 10 – manometer; 11 – hydrogen flow meter; 12 – shutoff valve;
13 – pressure regulating valve; 14 – thermostat; 15 – container with silicone tetrachloride ($SiCl_4$);
16 – pressure sensor of ВИТ-3 vacuum gauge; 17 – ВД-1 vacuum gauge; 18 – electronic scales;
19 – generator; 20 – interface unit

Measurements of voltage on the load circuit was carried out with the aid of a capacitance divider with dividing coefficient of 1000:1. Current in the inductor and the load circuit was measured with the aid of screened Rogowski coils.

The conducted modernisation permitted to gain low temperature non-equilibrium plasma into molecular hydrogen and into the mixture of hydrogen and silicon tetrachloride in the pressure range of … 250 Pa. Power density fed into high-frequency discharge was in the range of 1…7.2 W/cm^2.

In the experiments silicon tetrachloride of "ОС.Ч" [ultra pure] grade and hydrogen of "A" grade were used. To provide its stabilised flow rate the container with silicon tetrachloride were placed into the thermostat.

Before its supply to the experimental chamber hydrogen passed through nitrogen trap.

In the course of the experiments the following parameters were maintained constant: vapour-gas mixture pressure of 60 pascal, hydrogen flow rate of 6.5 l/hour, silicon tetrachloride ($SiCl_4$) flow rate of 10 g/hour, and power density fed into plasma of 6.5 W/cm^2. Temperatures of discharge chamber quartz tube wall were between 270 and 290 °C. Total duration of film deposition was 80 min.

The reaction of plasma chemical reduction ($SiCl_4 + 2H_2 = Si + 4HCl$) was carried out at $H_2/SiCl_4$ ratio equalled to 5/1.

As a result of the experiments made in the discharge zone on the internal surface of the quartz reaction chamber a deposition film was obtained.

From measured film thickness of 11.6 µm it followed that average rate of film growth, R_0, was equal to 2.41 nm/s. This significantly outnumbered the rates achieved in capacitive RF discharges.

To identify the film obtained X-ray diffraction phase-shift analysis was pursued. X-ray photography was made on ДРОН 4-07 X-ray diffractometer in CuK_α radiation at the Bragg-Brentano scheme with the pair of Soller slits.

The conducted studies demonstrated that specimens obtained from evaporated film consisted of amorphous and crystalline components. According to positions of lines <111>, <220> and <311> of the crystalline component it was gotten the amount of lattice spacing of 0.5427…0.5432 nm similar to reference value of 0.5430 for crystalline silicon [12].

Phase composition of the obtained film was analysed with X-ray diffractometry in CuK_α (λ = 1/5405 Å) radiation. Average size of silicon bicrystall grains, δ, was calculated from the Scherrer formula on measured half-width of diffraction line corresponding crystall-lattice orientation <111>. Obtained values $\delta \approx 20$ nm agreed to results obtained when crystalline silicon film deposition was executed into capacitive RF discharge allowed into dichlorosilane (SiH_2Cl_2) diluted with hydrogen [13]. The volume part of film, X_c, containing nanocrystalline silicon determined from the ratio:

$$X_c = \frac{\sum J_{nkl}}{\sum J_{nkl\,\max}},$$

where $\sum J_{nkl}$ is the sum of integral intensities of three diffraction lines corresponding to crystall-lattice orientations as <111>, <220 >, <311>, and $\sum J_{nkl\ \max}$ is the sum of maximal expected intensities of the mentioned lines [14]. In the films investigated, X_c, amounted 53%.

The structure of silicone film surface is shown on Fig. 2.

Composition of film material was determined by analysing characteristic X-ray spectra obtained on “Jeol” JSM-840 scanning electronic microscope. The typical X-ray spectrum of nanocrystalline part of silicon film is shown on Fig. 3.

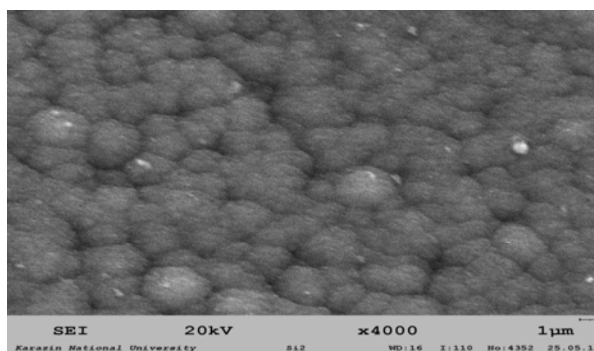

Fig. 2. The surface structure of silicon film

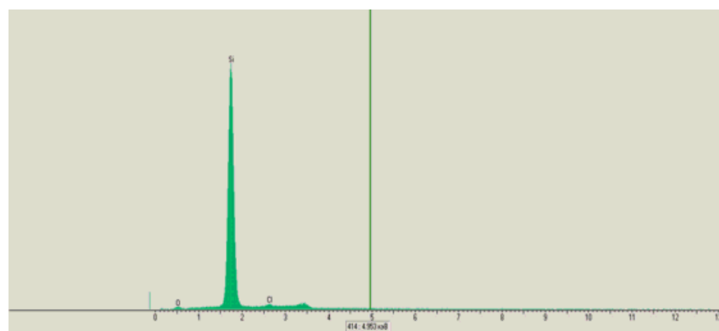

Fig. 3. Characteristic X-ray spectrum of nanocrystalline part of silicon film

Obtained nc – Si : H (Cl,O) silicon films contained 1.92 and 0.72% of Cl. Presence of oxygen in the film is attributable to gas emissions from adsorbed residue gases on the internal surface of the camera under baking during the experiment.

CONCLUSIONS

High rates of silicon film growth into low temperature non-equilibrium plasma of low frequency induction discharge were obtained. High rates of silicon film growth into low frequency induction RF discharge were caused by high level of dissociation of working mixture components into induction RF discharge plasma directly by the wall of discharge chamber. It can be supposed that increase in film volume part containing nanocrystalline silicone is possible under optimisation of substrate temperature and dilution rate of silicone tetrachloride by hydrogen.

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ОСАЖДЕНИЕ ПЛЁНОК НАНОКРИСТАЛЛИЧЕСКОГО КРЕМНИЯ В НИЗКОЧАСТОТНОМ ИНДУКЦИОННОМ ВЧ-РАЗРЯДЕ

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Представлены результаты исследований по получению пленок нанокристаллического кремния методом стимулированного плазмохимического осаждения (СПХО) в низкочастотном индукционном ВЧ-разряде (880 кГц), возбуждаемом в тетрахлориде кремния ($SiCl_4$), разбавленным водородом. Получена высокая скорость осаждения пленки кремния – 2,41 нм/с. Проведен рентгеноструктурный фазовый анализ, определена величина периода кристаллической решетки, исследована структура нанокристаллической пленки кремния.

ОСАДЖЕННЯ ПЛІВОК НАНОКРИСТАЛІЧНОГО КРЕМНІЮ В НИЗЬКОЧАСТОТНОМУ ІНДУКЦІЙНОМУ ВЧ-РОЗРЯДІ

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Представлено результати досліджень по одержанню плівок нанокристалічного кремнію методом стимульованого плазмохімічного осадження (СПХО) в низькочастотному індукційному ВЧ-розряді (880 кГц), збудженим у тетрахлоріді кремнію ($SiCl_4$), розведеним воднем. Одержано високу швидкість осадження плівки кремнію – 2,41 нм/с. Проведено рентгеноструктурний фазовий аналіз, визначено величину періоду кристалічної ґратки, досліджено структуру нанокристалічної плівки кремнію.

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