Si Thin Film Deposition from Free Jet of Argon-Silane Mixture Activated by Electron Beam[1]

S.Ya. Khmel, E.A. Baranov, and S.Z. Sakhapov

Institute of Thermophysics SB RAS, 1, Academic Lavrentiev ave., Novosibirsk, 630090, Russia
Phone: +7(383) 335-66-76, Fax: +7(383) 330-84-80, E-mail: khmel@itp.nsc.ru

Abstract – Silicon thin films are deposited by a gas jet CVD method with electron beam activation from an argon-silane mixture. The parameters of the electron beam plasma (temperature, density) were measured with the help of single electrostatic probes. The film deposition rate increases with the increasing of Ar flow rate and fixed SiH_4 flow rate. The plasma density increases in the same conditions, but the plasma temperature changes slightly. It is shown, that the main reason of the deposition rate increasing under increasing of the Ar flow rate consists in the rise of concentration of fast secondary electrons under the electron beam scattering. Namely, fast secondary electrons contribute main part in the SiH_4 dissociation, but not metastable atoms of argon. Electron beam plasma distinctly distinguishes from discharge plasma where metastable atoms of argon contribute enough part in SiH_4 dissociation in the argon-silane mixture.

1. Introduction

Various methods for plasma-enhanced chemical vapor deposition (PECVD) of thin amorphous and crystalline silicon films from plasmas of mixtures of monosilane (SiH_4) with diluent gases are widely used in microelectronics and semiconductor industry to produce thin-film transistors and solar cells [1, 2]. The most common diluent for monosilane is argon.

Usually intensification of deposition process in silane plasma conducts to generation of silicon nanoparticles and powder. If these nanoparticles fall onto surface of growing film, then they worsen film performance. Silane dilutes with inert gas (as a rule, with argon) for suppression of particle generation reactions [3, 4]. Using of diluent gas results in some increasing of deposition rate, but also defect density increases. Gas phase investigations show that the argon is not only buffer gas, suppressing reactions between radicals and silane molecules, but it plays active role in silane dissociation because of influence of argon metastable atoms [4].

In the past decade, gas jet CVD method with electron beam activation strongly develops [5, 6]. Fig. 1 presents scheme of the method. Main advantages of the method are next ones: the electron beam plasma contains much more high energy electrons (they are necessary for radicals and ions generation) than a discharge plasma, a fast convective transfer of active particles from the activation zone to the substrate by the jet inhibits undesirable gas-phase processes, at last the jet protects the substrate from the atoms and molecules of background gases. As a result, it allows growing thin films with high deposition rates and low power inputs in standard vacuum chambers under low vacuum conditions.

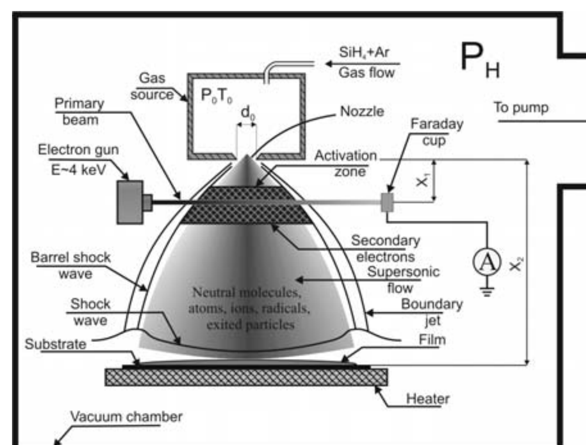

Fig. 1. Scheme of gas jet electron beam plasma CVD method

The main difference is that, in gas-discharge plasmas, the electron energy distribution function (EEDF) exponentially decreases with increasing electron energy and is vanishingly small at energies higher than the threshold energy for monosilane dissociation. In an electron-beam plasma, the EEDF forms in the course of energy degradation of the primary beam electrons and the secondary electrons produced via gas ionization by the primary electrons. In such a plasma, the high-energy tail of the EEDF decreases slowly with energy and there are a lot of electrons with energies corresponding to the maxima in the monosilane excitation cross section; hence, the gas is activated and monosilane molecules are dissociated more efficiently than in gas-discharge plasmas.

The aim of the paper consists in investigation of diluent gas effect on silicon film deposition processes from argon-silane mixture by the gas jet CVD method with electron beam activation.

[1] The work was supported by RFBR (Grant No. 08-08-00605).

2. Experiment

The experiments were performed in a low-density gas-dynamic setup at the Institute of Thermophysics of the Siberian Branch of the Russian Academy of Sciences. The setup is pumped out with a fore-vacuum pump. The background pressure was 2 Pa, pressure in vacuum chamber increased up to 9 Pa with feeding processing gases. Processing gases were argon and 5% mixture silane in argon. Gas feed system allowed using both gases simultaneously, gas flow rate monitoring was carried out by gas rotameters (Brook Instruments). The total gas flow may change from 50 sccm to 500 sccm (standard cubic centimeter per minute, here cubic centimeter refers to a cubic centimeter of the gas at $T = 273$ K and $p = 101, 325$ Pa). The gas came into the chamber through nozzle with diameter 2 mm. The pressure in the nozzle prechamber was measured using a capacitance manometer. The distance between nozzle and substrate holder was 20 mm.

The setup was equipped by a forepump electron gun with a plasma cathode, similar to one described in [7]. In comparison with thermo-cathode electron guns, the plasma cathode device has several advantages: the influence of reactive gases and reverse ion flow is uncritical; the plasma cathode gun works in fore-vacuum pressure region and mechanical pumping is enough. It allows generating electron beams with energy 0.5–4 keV and current up to 50 mA under background pressure up to 9 Pa. The electron beam diameter was 6–7 mm.

The substrates used for deposition Si films were n-type (100)-oriented Si wafers with SiO_2 layer (diameter 76 mm). The film thickness was measured in accordance with reflection spectrum in near IR region.

The parameters of the electron beam plasma (temperature, density) were measured with the help of single electrostatic probes. Probe was placed on crossing of gas jet axis and electron beam. Voltage-current characteristics of the electrostatic probes were recorded with help digital oscillograph (TDS 3034B, Tektronix).

3. Results and discussion

Figure 2 presents dependence of the silicon film deposition rate on the argon flow rate under a fixed silane flow rate. The gas flow rate varied from 80 to 330 sccm, correspondingly the silane concentration in the mixture decreased from 5 to 1.2%. It can be seen from Fig. 2 that the silicon film deposition rate increased from 0.37 to 0.56 nm/s, approximately in 1.5 times more. Moreover, deposition rate quickly ran up to saturation. Apparently, it connects with the circumstance that the electron beam heavy scattered on the background gas. Hence, the effect of the deposition rate increasing may be more evident under higher electron beam energy (and lesser scattering of the beam, accordingly). In the experiment the value of the electron beam energy was selected to achieve maximum of the deposition rate. Increasing of the deposition rate with increasing of the argon flow rate may be caused by growing of the fast secondary electron concentration or growing of the metastable argon atom concentration.

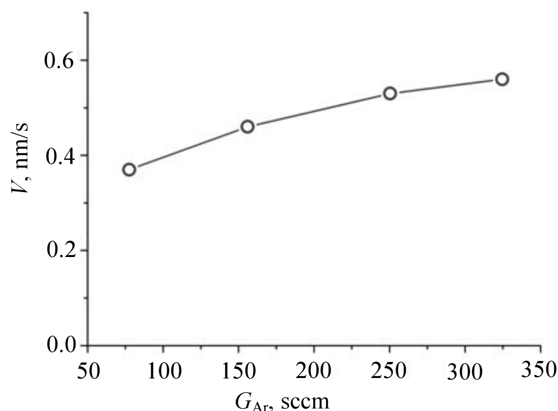

Fig. 2. Dependence of the silicon film deposition rate on the argon flow rate. The silane flow rate is 4 sccm. The electron beam energy is 1 keV, the current is 10 mA

To verify the assumption about influence of the fast secondary electrons on the process temperature and density of the plasma electrons were measured with help of single electrostatic probes. Densities of the fast secondary electrons and the plasma electrons are related.

The plasma electron temperature versus the argon flow rate is presented in Fig. 3.

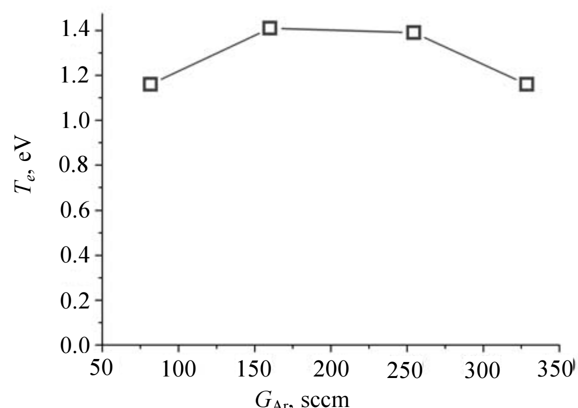

Fig. 3. Dependence of the plasma electron temperature on the argon flow rate. The electron beam energy is 1 keV, the current is 10 mA

In the experiment, the pure argon without silane is used because a small addition of silane in argon has slight influence on the electron beam scattering. The electron temperature changes slightly under increasing of the gas flow rate. It is usual behavior of electron temperature in an electron beam plasma under variation of gas flow rate (density) [8]. One can suppose that the electron temperature increases a little when electron beam begins to be scatter and decreases a little when the electron beam is scattered totally.

The plasma electron density depending on the argon flow rate as presented in Fig. 4.

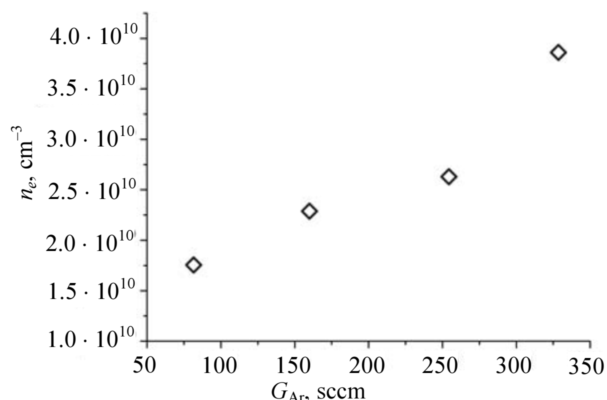

Fig. 4. Dependence of plasma electron density on argon flow rate

It can be seen from Fig. 1 that the plasma electron density increases with growing of the gas flow rate. Similar results were obtained in [8]. The plasma electron density unambiguously related with the fast secondary electron density, therefore one can say that the secondary electron density increases with increasing gas flow rate because of scattering of electron beam. Therefore growing of the fast secondary electron concentration is the reason of deposition rate increasing. However, it is obvious, that the argon metastable atom concentration also grows with increasing of the gas flow rate (density) because of scattering of the electron beam.

Mathematical modeling of electron beam activation of the gas mixture of silane and argon under low density by low current electron beam [9] shows that for electron beams with energy ($E \geq 1$ keV) namely secondary electrons give main contribution in gas dissociation because of energy structure of excitation cross sections of atoms and molecules by electron impact.

In Fig. 5, the dependence of dissociation frequency on the dimensionless penetration length $zN_g\sigma_0$ is presented for constant density of SiH_4 with different additions of argon [9]. Here, the monosilane density was kept constant, whereas the argon density was increased so that the SiH_4 concentration decreased from 10 to 1%. It can be seen that the dissociation caused by the primary beam electrons depends only slightly on the argon density. Minor variations in the rate of dissociation by primary electrons with increasing argon density are related to a change in the distribution function of the beam electrons because of the beam degradation. At the same time, the rate of SiH_4 dissociation by secondary electrons is seen to increase significantly with argon density.

Numerical calculations of radial profiles of the densities of slow plasma electrons and metastable argon atoms for gas densities of $N_g = 10^{15}$ and 10^{14} cm^{-3} are shown in Fig. 6 [9]. The main channels for the generation of metastable argon atoms are electron impact of argon atoms by primary beam electrons and fast secondary electrons.

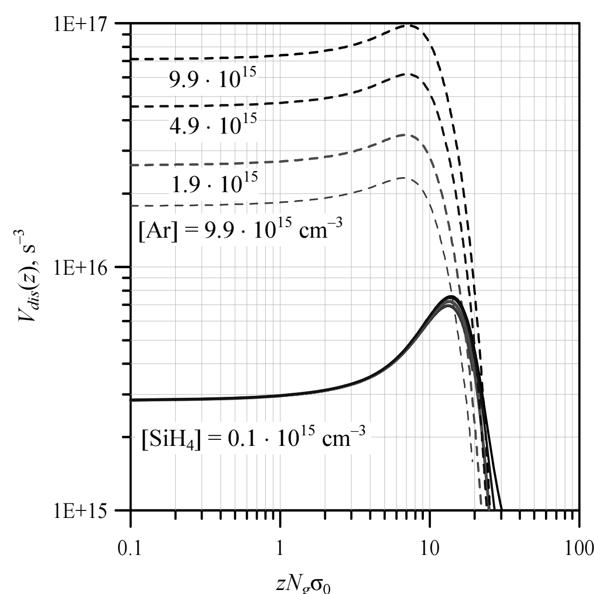

Fig. 5. Contributions from secondary electrons (dashed curves) and primary electrons (solid curves) to the rate of electron-impact dissociation vs. dimensionless penetration depth $zN_g\sigma_0$ of the beam electrons into the gas at a constant monosilane density ($N_{SiH_4} = 10^{14}$ cm^{-3}) and different argon densities corresponding to monosilane concentrations from 1 to 10%. N_g – gas density, $\sigma_0 = 10^{-16}$ cm^{-2}

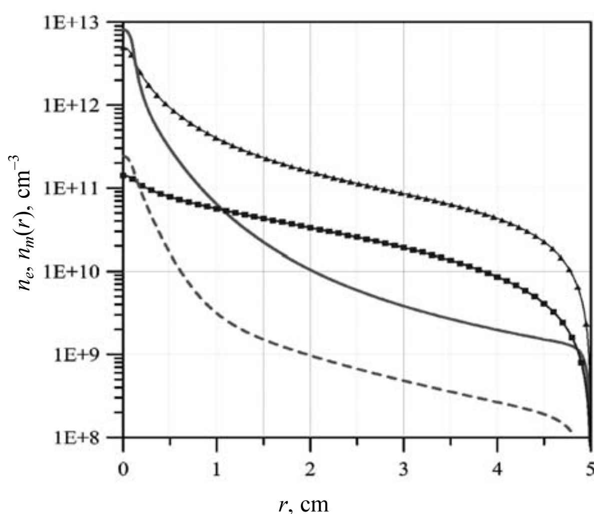

Fig. 6. Radial profiles of the densities of slow electrons at $N_g = 10^{15}$ cm^{-3} (triangles) and 10^{14} cm^{-3} (squares) and metastable argon atoms at $N_g = 10^{15}$ cm^{-3} (solid curve) and 10^{14} cm^{-3} (dashed curve) for $E = 1$ keV, diameter of electron beam 0.2 cm, chamber radius $R = 5$ cm, and 1% SiH_4 concentration

Rate of silane dissociation into neutral fragments were calculated on basis of data from Fig. 6. Numerical calculations of radial profiles of the rate of silane dissociation into neutral fragments are shown in Fig. 7. It can be seen that, within an electron beam, the

rate of SiH_4 dissociation by metastable particles can be comparable with (or can even exceed) the rate of electron-impact dissociation of silane.

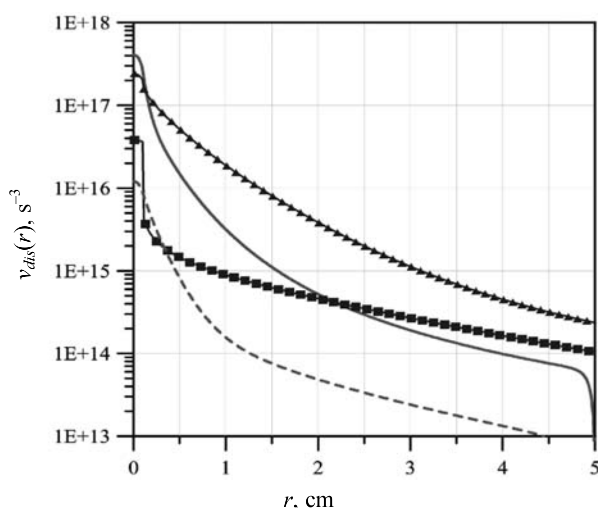

Fig. 6. Radial profiles of the rate of monosilane dissociation in collisions with electrons at $N_g = 10^{15}$ cm^{-3} (triangles) and 10^{14} cm^{-3} (squares) and with metastable argon atoms at $N_g = 10^{15}$ cm^{-3} (solid curve) and 10^{14} cm^{-3} (dashed curve) for $E = 1$ keV, diameter of electron beam 0.2 cm, chamber radius $R = 5$ cm, and 1% SiH_4 concentration

However, outside the beam, the density of metastable particles rapidly decreases due to their quenching in collisions with silane molecules, so the dominant process in this region is electron-impact dissociation of monosilane [9].

4. Conclusion

The effect of the buffer gas (argon) on the rate of SiH_4 dissociation into neutral fragments and silicon film deposition rate from an argon-silane mixture activated by electron beam has been investigated. It is shown that, at a constant density of SiH_4, the rate of monosilane dissociation and deposition rate increases with argon density (for SiH_4 concentrations in the range 1–10%). The parameters of the electron beam plasma (temperature, density) were measured with the help of single electrostatic probes in the same conditions. The plasma density increases (and the fast secondary electron density also), but the plasma temperature changes slightly. In experiments on the electron impact activation of argon–silane mixtures in RF discharges used to deposit thin silicon films, a similar effect was attributed to the influence of metastable argon atoms [4]. It is shown in the investigation, that this effect in the argon–silane mixture activated by electron beam plasma is mainly caused by the fast secondary electrons, but not metastable argon atoms. We have also studied the effect of metastable Ar* atoms on the dissociation of SiH_4 in an argon–silane plasma produced by an electron beam. It is shown that the efficiency of SiH_4 dissociation by metastable argon atoms can be comparable with the efficiency of direct electron-impact dissociation of SiH_4 within the electron beam. However, outside the beam, the density of metastable argon atoms decreases rapidly due to quenching collisions with monosilane molecules.

References

[1] A. Matsuda, Jpn. J. Appl. Phys. **43**, 7909 (2004).
[2] R.A. Street, Phys. Status Solidi A **166**, 695 (1998).
[3] J.C. Knights, R.A. Lujan, M.P. Rosenblum, R.A. Street, D.K. Bieglesen, and J.A. Reimer, Appl. Phys. Letters. **38**, 331 (1981).
[4] L. Sansonnens, A.A. Howling, Ch. Hollenstein, J.-L. Dorier, and U. Kroll, J. Phys. D: Appl. Phys. **27**, 1406 (1994).
[5] R.G. Sharafutdinov, A.V. Skrynnikov, A.V. Parakhnevich, B.M. Ayupov, A.M. Badolian, O.V. Polyakov, M.R. Baklanov, K.P. Mogilnikov, and S.A. Birykov J. Appl. Phys. **79**, 7274 (1996).
[6] R.G. Sharafutdinov, S.Ya. Khmel, V.G. Shchukin, M.V. Ponomarev, E.A. Baranov, A.V. Volkov, O.I. Semenova, L.I. Fedina, P.P. Dobrovolsky, and B.A. Kolesov, Solar Energy Materials & Solar Cells. **89**, 99 (2005).
[7] V. Burdovitsin and E. Oks, Rev. Sci. Instrum. **70**, 2975 (1999).
[8] V.O. Konstantinov and S.Ya. Khmel, J. Appl. Mech. & Tech. Phys. **48**, 1 (2007).
[9] G.I. Sukhinin, A.V. Fedoseev, and S.Ya. Khmel, Plasma Phys. Rep. **34**, 60 (2008).