

Novel approaches to plasma deposition of amorphous silicon-based materials

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Abstract - The effect of dopant addition, frequency of the r.f. field, UV-light irradiation, and plasma modulation on the plasma deposition of amorphous silicon based materials (a-Si:H, a-Si:H,F, a-Si,Ge:H,F) is examined. The discussion of the implications of the experimental results for current mechanistic models of these systems is stressed.

INTRODUCTION

Although the plasma-enhanced chemical vapor deposition (PECVD) of amorphous silicon films (a-Si:H, a-Si:H,F) and related materials (a-Si:Ge, a-Si:C, a-Si:N) is already used in the industry for solar cells and optoelectronic devices, considerable research efforts have been carried out, in the last few years, on some aspects which are still considered unsolved. In particular, the identity of the growth precursors, the plasma-surface interaction, and the microscopic parameters affecting the film quality are problems still debated in the scientific community (refs.1,2).

On the other hand, the progress in terms of industrial developments is still limited by serious gaps in the understanding and control of the material properties. Further important technological goals to be reached are: (a) the increase of the film deposition rate, for low cost production; (b) the improvement of the surface homogeneity, for the scaling-up process to large area devices; (c) the achievement of the topmost material quality, for high efficiency and stable devices (refs.3,4).

To give answers to the above open questions and to achieve the technological goals, two different approaches are normally used. First, the optimization of the process and material is carried out by acting on the external macroscopic plasma parameters (r.f. power, deposition temperature, gas pressure, feed composition, and reactor geometry). Second, the role played by internal plasma microscopic parameters (electron density and temperature, density of neutral and ionic species, etc.) on the deposition process and on the material quality is investigated.

Recently, some workers have addressed their attention to the study of novel growth methods in which unusual parameters, such as frequency of r.f. field (refs.5,6), plasma confinement (both magnetic and electrostatic) (ref.7), light irradiation (refs.8,9), and plasma modulation (refs.10-12), are involved, and/or higher silanes (Si_2H_6) and different reactor configurations are used. The common target which has characterized the development of these "new" methods is, for obvious reasons, the increase of the film deposition rate while keeping good material properties. In addition, some of these new parameters are emerging as tools to understand the deposition chemistry and to better define some fundamental properties of the material. For instance, A. Matsuda (ref.13) has used a triode glow discharge method to separate the plasma from the substrate region and select the specific radicals able to reach the growth surface. He found arguments for discussing the growth mechanism and for suggesting a "guiding principle" to obtain high quality Si-based alloys.

In this paper, we will analyze the above mentioned problems on the base of some recent studies on the effect of: (a) dopant addition (B_2H_6 , PH_3), (b) frequency of r.f. field (13-75 MHz), and (c) plasma modulation (10-100 Hz) on the deposition of amorphous silicon and silicon-germanium alloys from $\text{SiH}_4\text{-H}_2$, $\text{SiF}_4\text{-H}_2$ and $\text{SiF}_4\text{-GeH}_4\text{-H}_2$ systems, respectively. Some preliminary considerations on the effect of UV light irradiation will also be presented. Results on plasma diagnostics obtained mainly by Langmuir electrical probes (LEP) and optical emission spectroscopy (OES), also time-resolved (TROES), will be reported. It will be shown that: (a) the chemisorption process of the reactants (SiF_4 , GeH_4 , SiH_4), also of dissociative type, plays a relevant role in the surface growth kinetics; (b) the anatomy of the plasma, i.e. the spatial distribution of the glow between the electrodes, is a key factor in controlling the deposition rate when frequency is

varied; (c) film growth dishomogeneity, associated to the concentration gradients in the gas phase, can be strongly reduced under plasma modulation conditions; (d) time resolved optical emission spectroscopy (TROES) applied to modulated plasmas is a powerful tool to provide information on the origin of emitting species and to study the kinetics of the same species in their ground state.

DOPANT EFFECT. A TOOL EVIDENCING CHEMISORPTION

One of the common objectives of the research groups working in the field of amorphous silicon deposition is to provide a deposition model able to describe the surface growth from the kinetic point of view, i.e. to define the relationship between deposition rate and the species concentration in the gas phase. The debate on this theme is still lively and, in order to identify the growth precursors, the discussion has been centered, in these last years, on the most abundant silicon radicals in the plasma phase, sometimes regardless of their interaction with the growth surface (refs.1,2,14). This last aspect is, in our opinion, extremely important and merits to be debated, since a large amount of evidence exists, showing that plasma-surface interaction in both etching and deposition processes invariably involves the chemisorption of atoms, radicals and/or reactant molecules (refs.15-18). The general problem of chemisorption is therefore of fundamental importance in connection with the study of the chemical and kinetic phenomena occurring on the surface. With this respect the present discussion will be confined to those aspects which have particular relevance in connection with the role played by n- and p-doped materials on the kinetics of surface reactions.

It is well known that the addition of phosphine (PH_3) and diborane (B_2H_6) as dopant gases in the feed, during the deposition of n- and p-doped amorphous silicon, strongly affects the rate of material growth. However, they act in opposite way, also depending on the kind of silicon volatile reactants. This is well illustrated in fig.1, where typical data for amorphous silicon deposition are summarized. The main feature is the opposite behaviour of halogenated feed (SiF_4 , SiCl_4) with respect to hydrogenated feed (SiH_4). Similar results have also been observed for the growth of silicon from SiH_4 and Si_2H_6 under no plasma conditions. It is clear from these results that a sort of electronic interaction between molecules and surface must be invoked. Thus it could be helpful to refer to the model of chemisorption on semiconductor surfaces, which utilizes the boundary-layer theory (ref.19). According to this model, the chemisorption of halogenated reactants is promoted by n-doped surfaces and that of hydrogenated reactants by p-doped surfaces. These two possibilities are currently reported as anionic and cationic chemisorption (ref.20) on n- and p-doped materials, respectively. In the first case (anionic), there is an electron transfer from the donor levels of n-doped surface to the adsorbed molecule, leading to the correspondent anion. In the second case (cationic), the adsorbed molecule transfers an electron to the acceptor levels of p-doped surface, becoming a cation.

This model is strongly supported by the observation that in a-Si,Ge:H,F film deposition from SiF_4 -GeH₄-H₂ mixture, the partial deposition rates of silicon (r_{Si}) and germanium (r_{Ge}) have opposite behaviour with dopant addition, as illustrated in fig. 2. This result has to be expected, since silicon and germanium come from halogenated (SiF_4) and hydrogenated (GeH_4) reactants, respectively.

In addition, we have shown in previous studies on the deposition of a-Si:H,F and a-Si:H,Cl (from SiF_4 -H₂ and SiCl_4 -H₂ mixtures), that the occurrence of a dissociative chemisorption of the reactants (SiF_4 , SiCl_4)

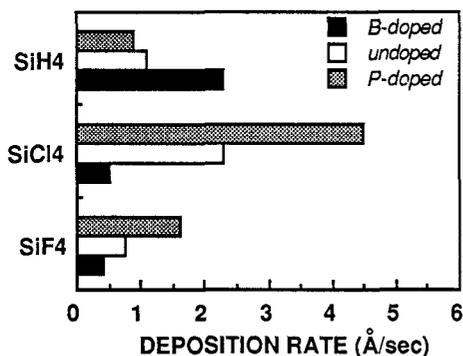


Fig.1. Stick diagram of the doping effect on the silicon film deposition rate for the SiH_4 , SiCl_4 , and SiF_4 systems.

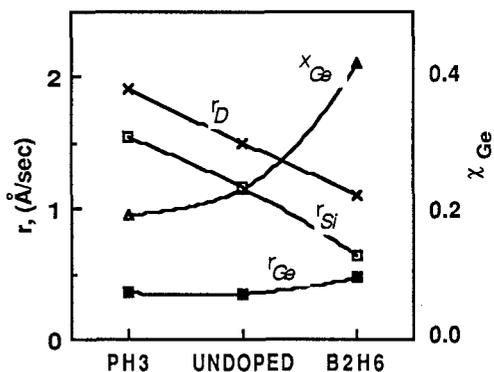
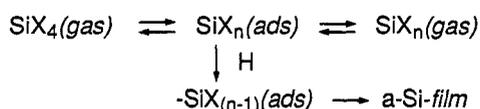


Fig.2. Total deposition rate (r_D), Si and Ge partial deposition rate (r_{Si} , r_{Ge}), and Ge content (x_{Ge}) for undoped and doped a-Si,Ge:H,F films from SiF_4 -GeH₄-H₂ plasmas.

can allow the salient experimental findings to be probed and understood (refs.18,21). A simplified scheme of our suggested deposition model can be drawn as follows:



The importance of the dissociative chemisorption process is strongly supported by the well known activated dissociative chemisorption mechanism of Lennard-Jones, which has been recently reviewed by S.T. Ceyer (ref.22). For the sake of space, we can not enter into the mechanism details; nevertheless two aspects are worth mentioning:

- a- the collisional energy (both translational and vibrational) of an incident molecule has been proved to be effective to surmount the dissociation-activation barrier, and hence to strongly increase its probability;
- b- the collision of energized species (atoms, radicals) coming from the plasma phase with adsorbed molecules results in their dissociation (collision-induced dissociation).

In conclusion the study of the dopant effect on the growth kinetics has revealed to be effective in evidencing and clarifying the plasma-surface interaction. In particular, it has shown that the chemisorption of reactants (SiH_4 , SiF_4 , SiCl_4) is the most important process to bring silicon on the surface. The role of the plasma is double: (a) to supply internal energy to adsorbed molecules, which can potentially dissociate on the surface, and (b) to produce energetic species, which like a hammer collide with adsorbed molecules, giving energy for their dissociation.

PHOTOEFFECT ON DEPOSITION RATE

Although it is well known that the light irradiation considerably affects the gas-surface interaction, its application to plasmachemical systems has not attracted sufficient attention.

The importance of this 'new' topic in the amorphous silicon deposition derives from the peculiarity of the semiconducting materials, when irradiated with above-gap light, to promote carriers in the conduction band and hence to modify the local electronic structure and charge distribution at the surface. This has been well illustrated by F.A. Houle (ref.23), who studied the effect of visible light on the etching reaction of intrinsic and doped silicon with XeF_2 under no-plasma conditions.

The role of UV light irradiation as a parameter affecting the plasma-surface interaction has been investigated, in our laboratory, during the deposition of a-Si:H films from $\text{SiH}_4\text{-H}_2$ mixtures. The deposition surface has been irradiated with UV light (Hg lamp) under typical experimental conditions for good quality materials ($\text{SiH}_4\text{:H}_2 = 1:9$, $\Phi_t = 20\text{sccm}$, $p = 0.3\text{ torr}$, $T_n = 300^\circ\text{C}$).

Light irradiation of the surface results in the following findings:

- the optical emission intensities of Ar^* (line at 750.4 nm) and H^* (line at 656.3nm) show an increase of about 5% with respect to those in absence of UV irradiation;
- the film deposition rate increases under UV-irradiation. The amount of this variation depends on the discharge power and reaches its maximum at 10watts where the deposition rate increases from 0.7 to 1.4 Å/sec
- the powder formation in the gas phase, i.e. the efficiency of the nucleation processes, strongly increases under UV-irradiation conditions.

These findings can be explained on the basis of two phenomena:

- electron photo-detachment,
- chemisorption photo-enhancement.

The former refers to the detachment of electrons from negative ions, and accounts for the increase of Ar^* and H^* intensities as these are related to the density of resonant electrons in the excitation processes.

The latter refers to the fact that light irradiation can have an 'amphoteric' effect on the interaction of molecules with silicon surface, in the sense that the generation of electron-hole pairs can stimulate both cationic and anionic chemisorption. An acceptor-like molecule (SiF_4 , SiCl_4) captures an electron and converts into anionic state (SiF_4^- , SiCl_4^-), thus charging the surface positively, while a donor-like molecule (SiH_4 , GeH_4) captures holes, thus converting to cation (SiH_4^+ , GeH_4^+) which interacts with a negatively charged surface.

The third experimental evidence (powder formation) can be explained by the model suggested by M.L.Mandich et al. in SiD_4 system(ref.24), which is based on the following points:

- the initial clustering reactions require positive ions to react with SiD_2 up to a maximum of three stepwise additions; further cluster growth proceeds only through chemisorption of SiD_4 (and presumably SiH_4) on large silicon clusters, analogously to chemisorption on silicon surfaces.
- negative ion clustering reactions are extremely slow, $<0.05\%$ of the ion-molecule collision rate;
- neutral-neutral clustering may lead to particle formation.

The concurrence of the above two phenomena, in presence of light irradiation, positively affects the nucleation process because of the decrease of negative ions, which are cluster terminators, and of the activation of the SiH_4 chemisorption on bare clusters.

As regarding the influence of light irradiation on the material properties, very few and contradictory results have been so far reported (refs. 8,9). In general, hydrogen incorporation, microcrystallinity, dark- and photo-conductivity, and stability to long light exposure are affected.

The suggestion that can be drawn from these preliminary results is that light irradiation negatively affects the deposition process.

FREQUENCY EFFECT: A MODIFICATION IN PLASMA ANATOMY

The exploitation of the excitation frequency, ω , as a processing parameter for etching and deposition is one of the recent developments in plasmachemistry (ref. 5,25,26). The aim is to define the "optimum" frequency of the plasma leading to the most efficient process.

On this subject, a review treating the problem from the theoretical and experimental point of view has been published by the research groups of C.M. Ferreira, J. Paraszczak and M. R. Wertheimer (ref.27). The main conclusion, accounting for their experimental results on the effects of frequency in both plasma deposition and etching of polymer films, deals with the influence of ω on the shape of electron energy distribution function.

The same conclusion has been drawn by H.Curtins et al. (ref.5), which primarily have reported the investigation of a-Si:H deposition from pure SiH_4 at different RF frequencies in the range 13-150 MHz. They found that around 75 MHz the deposition rate reaches its maximum value, a factor of 5-8 higher than at standard industrial frequency (13.56 MHz).

In addition, the excitation frequency has been found to affect other discharge characteristics (ref.25) (spatial distribution of the electrical field, time fluctuation of energy and density of species during the oscillation period of the applied field, minimum voltage required to sustain the plasma), which can be determinant in controlling the physics and chemistry of the plasma process. Among these, the effect on the spatial distribution of the species (both neutral and charged) and electrical fields between the electrodes is extremely important, since variations of electron density, n_e , and energy, $\langle e \rangle$, by a factor of ten or more with position have been found to occur in parallel plate plasma reactor for a-Si:H film deposition. With this respect we have recently investigated the plasma deposition of a-Si:H from $\text{SiH}_4:\text{H}_2$ (1:9) mixture at three different RF frequencies (13,27,75 MHz). Emphasis has been given on the spatially resolved diagnostics with Langmuir electrical probes. The resulting data of deposition rate, measured as a function of the rf power, and of electron density, n_e , and mean energy, $\langle e \rangle$, measured at different positions in the plasma, are summarized in Figs.3,4.

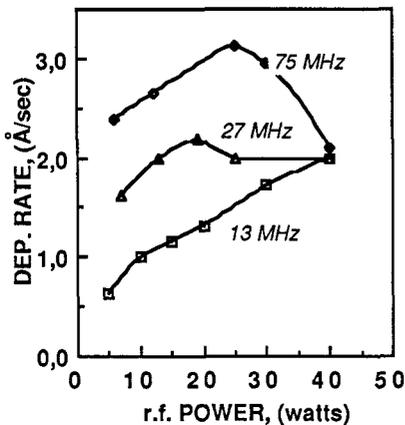


Fig. 3 Deposition rate of a-Si:H films from $\text{SiH}_4\text{-H}_2$ plasmas at three different r.f. frequencies as a function of r.f. power.

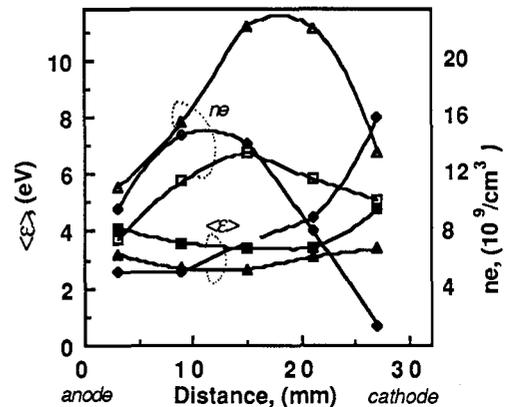


Fig.4 Mean electron energy, $\langle e \rangle$ and electron density, n_e , profiles measured in Ar plasma at 13 (\bullet, \diamond), 27 ($\blacktriangle, \triangle$) and 75 (\blacksquare, \square) MHz. ($p=0.3\text{torr}$, $W=10\text{ watt}$, $\Phi_{\text{Ar}}=10\text{sccm}$)

The observed increase of r_D with frequency confirms the results obtained by H.Curtins et al. (ref.5). As for the anatomy of the plasma, it can be noted that the 13 MHz plasma is characterized by a large asymmetrical dishomogeneity in both $\langle e \rangle$ and n_e values, which is also associated with a very thick sheath at the powered electrode. At higher frequency $\langle e \rangle$ and n_e profiles are smoother and the cathodic sheath correspondingly becomes very thin. The fact that the plasma becomes more energetic near the grounded deposition electrode seems to be the key factor accounting for r_D increasing with frequency.

As for the material characterization, films grown at similar deposition rate and different frequencies have been compared, in order to isolate the frequency effect from those due to surface kinetics. Preliminary results have shown no difference among them. Typical data for samples deposited at 0.9 Å/sec are as follows: dark conductivity= $10^{-12} \Omega^{-1}\text{cm}^{-1}$, photo-to-dark conductivity ratio (AM1)= 5×10^6 , γ -factor($\sigma_{PH} = I$)=0.92, optical gap=1.83 eV, conductivity activation energy=0.92eV, hydrogen content=18 at.%.

PLASMA MODULATION: A CHANCE TO IMPROVE MATERIAL PROPERTIES, PROCESS AND ITS DIAGNOSTICS

Plasma modulation is a relatively new approach to PECVD of amorphous silicon based materials, which has been utilized to enhance deposition rate (refs.10,11), material quality (ref.12), and surface uniformity (ref.28) and to suppress powder formation (refs.11,29).

A modulated wave (MW) discharge is characterized by a periodical switching on and off of the plasma, so causing completely different conditions in comparison to the continuous wave (CW) discharges.

In addition, plasma modulation can be utilized, when coupled with a time resolved diagnostics, as a method for measuring the formation and decay rates of radicals. This is well illustrated in fig.5, where the time resolved-optical emission spectrum (TR-OES) in the region 200-500nm for SiF₄-H₂ plasma is reported.

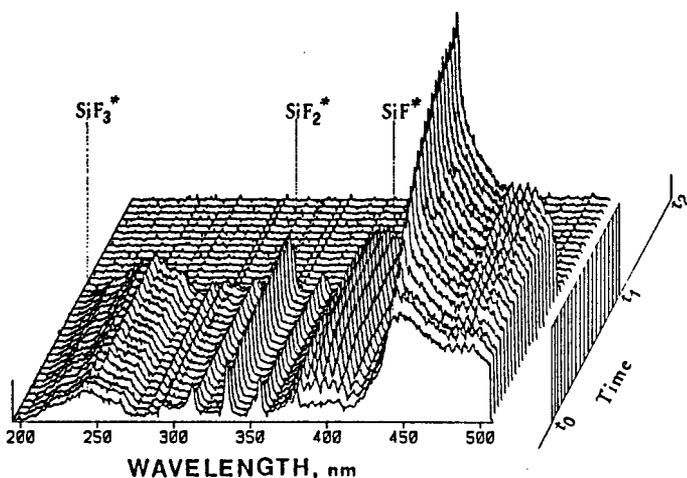


Fig.5. Temporal evolution of the optical emission spectrum in SiF₄:H₂:Ar (10:1:0.1) modulated plasma (period=10ms, D.C.=50%) at 27 MHz, p=0.3torr, $\Phi=11\text{sccm}$, W=20watt.

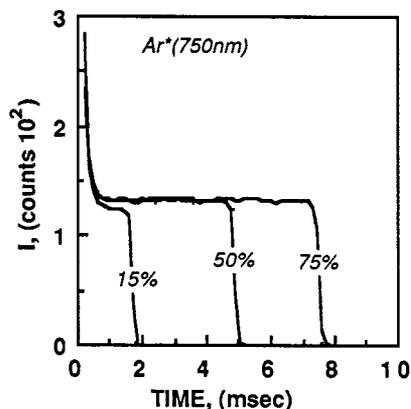


Fig.6. Temporal evolution of Ar* emission intensity in modulated plasmas at different duty cycles and fixed period of 10msec (other conditions as in Fig.5).

The morphology of the MW plasma can be described by means of the Ar emission intensity profile (see Fig. 6) which is representative of the fractional density of electrons with energy higher than 13.5 eV. In this profile three different regions can be distinguished: (a) a transient region, TR, where the Ar* emission intensity strongly changes through a well shaped maximum, reaching its stationary value after few tenths of msec. In this first region the transient electron temperature is very high and decreases toward the steady state value (CW value), while the total electron density is increasing (ref.12) (b) a stationary region, ST, where the Ar* emission intensity is practically constant and, hence, the electron density and temperature reach their stationary values (CW conditions); (c) an afterglow region, AG, where the Ar* emission intensity rapidly decays reaching its zero value and all the species produced in the plasma (ST and TR regions) decay according to their life time values. The analysis of the temporal evolution profiles of the emission lines can give some highlights on the origin of the emitting species and on their formation and decay kinetics. Fig.7 shows the typical time dependent profiles of SiF* intensity in MW-plasmas of SiF₄-H₂-Ar mixture. Similar profiles have also been recorded for SiF₂*, SiF₃* and H* emitting species. On the contrary, for SiH₄-H₂ and SiF₄-GeH₄-H₂ plasmas the Si*, SiH*, Ge*, GeH* and H* profiles resemble that of Ar* in Fig. 6. The explanation is that SiF_x* takes origin from a direct excitation of SiF_x in the ground state, while Si*, SiH*, Ge*, GeH* originate from a dissociation-excitation process of SiH₄ and GeH₄, respectively. Hence, the SiF_x* profiles are representative of SiF_x formation kinetics (because of the constancy of Ar emission intensity in ST-region) and their decay in the AG-region can be derived as illustrated in Fig. 8. Besides the diagnostic aspects, plasma modulation is a powerful tool to improve processes and material properties.

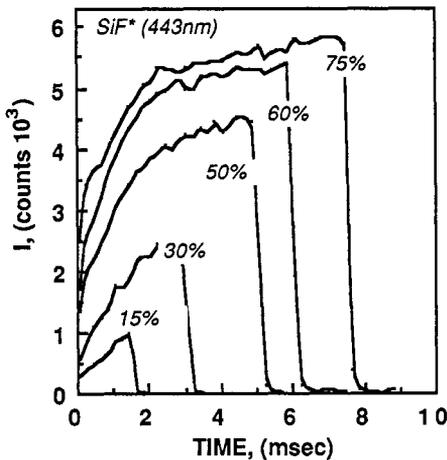


Fig. 7. Time dependence of SiF* emission intensity in modulated plasmas at different duty cycles and fixed period of 10ms (other conditions as in Fig. 5)

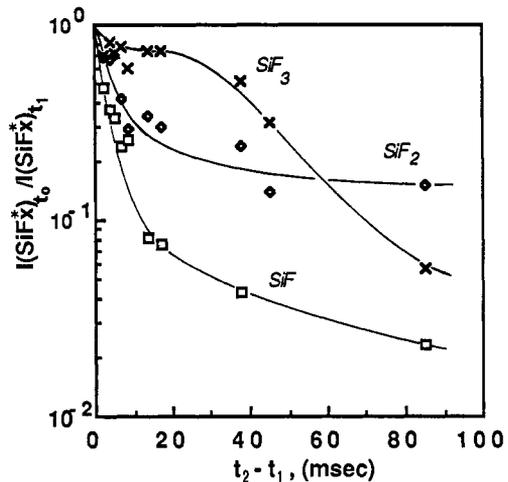


Fig. 8. Decay of SiF₃, SiF₂, and SiF radicals ($I(\text{SiF}_x)_{t_0}/I(\text{SiF}_x)_{t_1}$) in the afterglow region (t_2-t_1) of SiF₄:H₂:Ar modulated plasmas (t_0 , t_1 and t_2 refer to the points indicated in Fig. 5)

This is particularly true for those systems, such as SiF₄-H₂ (ref.28), SiF₄-GeH₄-H₂ (refs.28,29) and all binary systems for the deposition of silicon alloys, in which the density gradients of reactive species in the plasma phase imply a surface dishomogeneity in the film thickness (ref.31) and in material composition and properties (ref.30). As an example, a-Si:H,F films deposited in typical MW-discharge exhibit a photo-to-dark conductivity ratio one order of magnitude higher ($\approx 10^6$), than that for sample deposited under CW-conditions ($\approx 10^5$).

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