Time evolution of the process of doping of solids by plasma-ion beams

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Abstract. Irradiation of a solid with intense plasma-ion beams produced by Rod Plasma Injector is a strongly nonequilibrium process, which enables achieving a number of effects which are impossible to be achieved with other methods – improvement of ceramics wettability, fabrication of stable copper-ceramics interfaces and stable Ni-Cu and Al-Cu interfaces, improvement of tribological properties and high temperature oxidation resistance of stainless steel, photovoltaic junction formation, and many others. In the paper, the process of plasma-ion beam propagation regarding its time and energy distributions and the process of ion penetration of solids, resulting with ion implementation and temperature growth have been analyzed mathematically on basis of experimental data. Results of numerical calculations have been presented concerning temperature and dopant density time evolution.

Keywords: plasma, ion beam, implantation, doping, time evolution, energy distribution, stopping power

Introduction

Irradiation of solids with so-called plasma-ion beams is a strongly nonequilibrium process, which enables a number of effects that are impossible to achieve with other methods [1]. These include improvement of wettability of ceramics [2,4,8], production of stable copper-ceramics interfaces [3], production of stable Ni-Cu and Al-Cu interfaces [10], improvement of properties of zirconium alloys [13], improvement of tribological properties of stainless steel [5], improvement of high temperature oxidation resistance of stainless steel [6], modification of superconducting and electrical properties of Mg–B structures [7], improvement of manganese distribution in Si with He⁺ and H⁺ plasma pulse irradiation [9], doping metals with nitrogen [11], and photovoltaic junction formation [12].

The concept of the so-called Rod Plasma Injector (RPI) was proposed by Michał Gryziński [14,15] and verified experimentally [16-19], including the recently set in operation IBIS-II RPI-type plasma generator [20]. The RPI is a very effective source of intense plasma-ion beams emitted in the form of short pulses of a duration of few microseconds, plasma density of the order of $10^{16}$ cm$^{-3}$, and ion energy distribution up to several hundreds of keV – see Figs. 1-2. The process of ion propagation was initially analyzed in lit. [22].
1. Ion-plasma beam propagation

A complete set of ion emitting source parameters must consist of the following data:

1. total number of ions,
2. ion energy distribution,
3. ion start time distribution.

For numerical calculations (whose results are presented at the final part of the article), the following input data have been used:

1. energy distribution \( f_\varepsilon(\varepsilon) \) has the form shown in Fig. 1,
2. ion start time distribution \( \Phi(\tau) \) has the form shown in Fig. 2,
3. having been accelerated within the plasma generator, ions move straightforward with uniform motion,
4. number of ions \( N_0 = 5 \times 10^{12} \text{ cm}^{-2} \),
5. target: silicon Si.

With initial conditions listed above, the total on-target energy density is about 0.08 J/cm².

An ion source can be understood as some surface \( \Sigma \), which emits ions in accordance with the energy distribution \( f_\varepsilon(\varepsilon) \), and time distribution \( \Phi(\tau) \).

To begin with, we will consider an elementary ion "microsource" stretched over a surface element \( d\Sigma \), emitting ions within a time interval \([\tau, \tau+\delta\tau]\) - see Fig. 3.
\[ \delta N = N_0 \frac{d\Sigma}{d\tau} \Phi(\tau) \ d\tau \]  

(1)

The number of ions emitted from the "microsource" with an energy within \([\epsilon, \epsilon + d\epsilon]\) is:

\[ dN = \delta N f_e(\epsilon) \ d\epsilon \]  

(2)

Ions move from the source to a target along trajectories which can be expressed in terms of kinetic energy \(\epsilon\), flight time \(\tau\), and position vector \(z\):

\[ \epsilon = \frac{mz^2}{2(t - \tau)^2} \]  

(3)

In order to obtain expressions for on-target observables, one must transform the energy function \(f_e\) into the respective time-of-flight distribution function at a fixed source-target distance:

\[ f_\tau(t - \tau, z) = \frac{f_e(\frac{mz^2}{2(t - \tau)^2})}{d(t - \tau)} = \frac{mz^2}{(t - \tau)^3} f_e(\frac{mz^2}{2(t - \tau)^2}) \quad (z = \text{const.}) \]  

(4)

Now, the number of particles (from the "microsource") filling the volume element \(dV\) within the time interval \([\tau, \tau + d\tau]\) can be calculated as:

\[ dN = N_0 \frac{d\Sigma}{d\tau} f_\tau(t - \tau, z) d(t - \tau) \Phi(\tau) d\tau \]  

(5)

Taking into account geometrical relations:

\[ \frac{dz}{d(t - \tau)} = \frac{z}{t - \tau} = v, \quad dV = dz \ dS \]  

(6)

we finally obtain the integral equation which connects ion source parameters with the on-target beam density:

\[ n = \frac{dN}{dV} \rightarrow n(t, z) = \frac{dN}{dV} = mN_0 \int_0^t \frac{z}{(t - \tau)^2} f_e(\frac{mz^2}{2(t - \tau)^2}) \Phi(\tau) d\tau \]  

(7)

The same can be done with flux and power:

\[ dJ = dN \nu = dN \frac{z}{t - \tau} \rightarrow J(t, z) = m N_0 d\Sigma \int_0^t \frac{z^2}{(t - \tau)^3} f_e(\frac{mz^2}{2(t - \tau)^2}) \Phi(\tau) d\tau \]  

(8)

\[ dP = \frac{dN \frac{dV}{d(t - \tau)} dS}{2(t - \tau)^2} \rightarrow P(t, z) = \frac{1}{2} m^2 N_0 d\Sigma \int_0^t \frac{z^4}{(t - \tau)^5} f_e(\frac{mz^2}{2(t - \tau)^2}) \Phi(\tau) d\tau \]  

(9)

The density of the energy deposited on a target is:

\[ E(z) = \int_0^t P(t, z) \ d\tau \]  

(10)
2. Time evolution of doping process

The formulae derived above enable a numerical model to be constructed, which enables an immediate evaluation of the on-target ion flux shape at hand. Henceforth, it is possible to compute an evaluation of the implantation process parameters.

To achieve this goal, one has to “filter” the ion beam flux formula (8) using the energy dependent Dirac delta function:

\[ j(\epsilon, t, z) = mN_0 \int_{-\infty}^{+\infty} J(t, z) \delta(\epsilon - \frac{mz^2}{2(t-\tau)^2})d\epsilon \]

From (11) we obtain, after some development, the time dependent energy distributed flux of ions approaching the target:

\[ j(\epsilon, t, z) = mN_0 \Phi \left( t - \sqrt{\frac{mz^2}{2\epsilon}} \right) f_{\epsilon}(\epsilon) \]

(12)

As seen above, the flux is elicited directly from ion source parameters, i.e. energy distribution, time distribution of the emission, and number of particles. An example of the flux of target approaching ions, computed at a series of time instants, is shown in Fig. 5.

Coupled with the parameters of the ion beam impinging the solid, formula (12) allows us to precisely compute details of the process of ion penetration of a target. As the result, we can
achieve time dependent in-depth distributions of densities of doping ions, as well as a full history of the temperature distribution resulting from the energy released by ion irradiation.

During the solid penetration process, the temporary position of the ion depends on the material parameters and initial energy. It can be calculated with stopping power data [22]:

$$z(\epsilon_0, \epsilon) = \int_{\epsilon_0}^{\epsilon} \frac{d\epsilon}{S(\epsilon)}$$

(14)

where: $\epsilon_0$ – initial energy value,
$\epsilon$ – local energy value,
$S$ – stopping power function.

From (14) we immediately get the ion doping depth:

$$z_{dop}(\epsilon_0) = z(\epsilon_0, 0)$$

(15)

Examples of a stopping power function shape of diverse ions penetrating a silicon wafer are shown in Fig. 6. An adequate dependence of the doping depth on the initial ion energy is shown in Fig. 7.

The above data makes it possible to estimate the duration of a single ion doping process:

$$\tau = 2 \delta \left(\frac{m}{\epsilon_0}\right)^{1/2} \approx 10^{-12} \text{s}$$

(16)

$\delta$ – penetration depth,
$\epsilon_0$ – initial energy,
$m$ – ion mass.

As seen above, the duration of the doping process is several orders of magnitude less than half of an ion pulse. Therefore, it can be assumed that the process of penetration, i.e. from impacting to stopping, is in fact an immediate one, „out of time”, within the actual time framework (on the order of 5 µs). This fact enables us to directly transform the initial energy of ions into an in-depth distribution. This can be done by an exchange of energy coordinate into position coordinate (prior to this, the reversed form of the function (15) must be found):

$$j(\epsilon_0, t) = j(\epsilon_0(z), t) \frac{d\epsilon_0(z_{dop})}{dz_{dop}}$$

(17)
From this, we can compute the in-depth dopant concentration:

\[ n(z, t) = \frac{dN}{dz_{dop}} = \int_0^t j(\epsilon_0(z_{dop}), \tau) \frac{d\epsilon_0(z_{dop})}{dz_{dop}} d\tau \]  \hspace{1cm} (18)

The calculated time evolution of a doping process is shown in Fig. 8.

Fig. 8. Left: time evolution of dopant density distribution. Right: final dopant density distribution (B' ions in silicon). Distance between plasma source and the target is 2 m.

3. Time evolution of temperature distribution

As shown by formula (16), the ion transfer from the surface to a certain position is much faster than the doping process time scale, therefore the position dependent ion energy loss depends solely on the initial energy of the ion. Therefore, the energy deposited at the ‘z’ position is the sum of energies of all ions approaching this position within the time interval \([t, t+dt]\).

Hence, the total energy transferred to a solid by a group of ions with the energy of \([\epsilon, \epsilon+\epsilon d]\) and time interval \([t, t+dt]\) at the position ‘z’ is equal to (the function \(\epsilon(z, \epsilon_0)\) is elicited from formula (14)):

\[ dQ(z, t, \epsilon_0) = dz \, dt \, j(\epsilon_0, t, d) \frac{d\epsilon(z, \epsilon_0)}{dz} \, d\epsilon_0 \]  \hspace{1cm} (19)

From (19) we immediately achieve the temperature time evolution:

\[ T_{ref}(z, t) = \frac{dQ}{\delta \gamma \, dz} = \frac{1}{\delta \gamma} \int_0^t dt \int_{\epsilon_0}^\epsilon j(\epsilon_0, t, d) \frac{d\epsilon(z, \epsilon_0)}{dz} \, d\epsilon_0 \]  \hspace{1cm} (20)

\(d\) – distance between source and target,
\(\delta\) – target stuff density,
\(\gamma\) – specific heat.

Expression (20) has an essential fault – it does not consider that the target substance melts. Consequently, it must be understood as only a sort of “reference temperature”, which gives the basis for the final procedure of the real temperature computation which contains the process of melting. Finally, calculation is as follows:
\[
T(z,t) = \begin{cases} 
T_{\text{ref}}(z,t) & \text{if } T_{\text{ref}} < T_{\text{melt}} \\
T_{\text{melt}} & \text{if } T_{\text{melt}} < T_{\text{ref}} < T_{\text{melt}} + \sigma_{\text{melt}}/\gamma \\
T_{\text{ref}}(z,t) - \sigma_{\text{melt}}/\gamma & \text{if } T_{\text{ref}} > T_{\text{melt}} + \sigma_{\text{melt}}/\gamma 
\end{cases}
\] (21)

\(T_{\text{melt}}\) – melting point,
\(\sigma_{\text{melt}}\) – melting heat,
\(\gamma\) – specific heat [23].

An example of calculation of in-depth temperature distribution is shown in Fig. 9.

**Fig. 9. Time evolution of temperature distribution (B⁺ in silicon).**

*Distance between plasma source and the target is 2 m.*

Final results of silicon wafer irradiation with plasma-ion beams consisting of diverse elements are shown in Figs. 10 and 11. As seen, parameters of doping processes with argon, boron, nitrogen, carbon, or fluorine ions are quite similar. At the same time, the hydrogen plasma reacts to silicon in quite a different way.

**Fig. 10. Final temperature distributions of silicon target irradiated with different ion beams.**
4. Energy dissipation

Accuracy of the presented model is disturbed by at least five dissipative processes: evaporation, infrared emission, heat flow, deionization and sputtering.

i. Evaporation

\[ \frac{\partial q}{\partial t} \approx p \sqrt{3kT/m} \approx 1.8 \times 10^{-3} \text{ J}/(\mu \text{s cm}^2) \]

\( p \) – equilibrium vapour pressure (Si: \( 10^4 \) Pa at 2700 °C) [25]
\( m \) – atom mass.

ii. Infrared emission

\[ \frac{\partial q}{\partial t} = \varepsilon \sigma T^4 \approx 2.3 \times 10^{-4} \text{ J}/(\mu \text{s cm}^2) \text{ (at T=2700 °C)} \]

\( \varepsilon \) – emissivity (Si: \( \varepsilon \approx 0.5 \) [24])
\( \sigma \) – Stefan-Boltzmann constant.

iii. Heat flow:

\[ \frac{\partial q}{\partial t} = -\lambda \frac{\partial T}{\partial z} \quad (22) \]

\( T \) – temperature,
\( q \) – heat flux,
\( \lambda \) – heat conductivity (Si: \( 148 \) W/(mK)).

The heat flux, evaluated on the basis of the heat flow equation (22) at the temperature gradient of ca. 200 K/\( \mu \)m (taken from Fig. 9), is:

\[ \frac{\partial q}{\partial t} \approx 3 \times 10^{-5} \text{ J}/(\mu \text{s cm}^2) \]

iv. Deionization

Fig. 11. Final dopant density distributions at silicon target irradiated with different ion beams.
Penetrating a solid body, ions are submitted to deionization process. Therefore they release the energy less or equal to their ionization potential:

\[ \frac{\partial q}{\partial t} \approx \varepsilon_i \frac{N_0}{\Delta t} \approx 5.8 \times 10^{-7} \text{ J/(\mu s cm}^2\text{)} \]

\( \varepsilon_i \) – ionization potential of boron: \( \varepsilon = 8.3 \text{ eV} \).

v. Sputtering

\[ N_{\text{sput}} = \varepsilon_s N_0 \approx 1.6 \times 10^{12} \text{ cm}^{-2} \quad (<1 \text{ atomic layer}) \]

\( \varepsilon_s \) – sputter yield, \( \varepsilon_s \approx 0.33 \text{, B:Si, 1-10 keV) [26]} \]

Within the analysed set of parameters sputtering process affects the solid surface within the extent of only 1 atomic layer, and therefore it can be regarded insignificant.

Taking into account that the incoming energy flux is on the order of \( 2 \times 10^2 \text{ J/(\mu s cm}^2\text{)} \), we may assume that the dissipative processes mentioned above are too slow to have a significant influence on the process of ion doping. However, above 2700 °C the influence of the evaporation heat flow (with a silicon target) is becoming indispensable.

**5. Conclusions**

Having the set of computation tools defined above, and within the assumed framework of initial parameters including energy distribution, emission pulse duration and pulse shape, number of ions, and the distance between plasma source and irradiated target, one can perform a credible comparison of doping processes of different ions. Further analysis will concern a significantly enlarged temperature (above 2500 °C) and time frames (from microseconds to milliseconds and more) in which the dissipative processes as well as dopant migration in the liquid phase of a solid will be taken into account.
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