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Publication Date

1994-07-01



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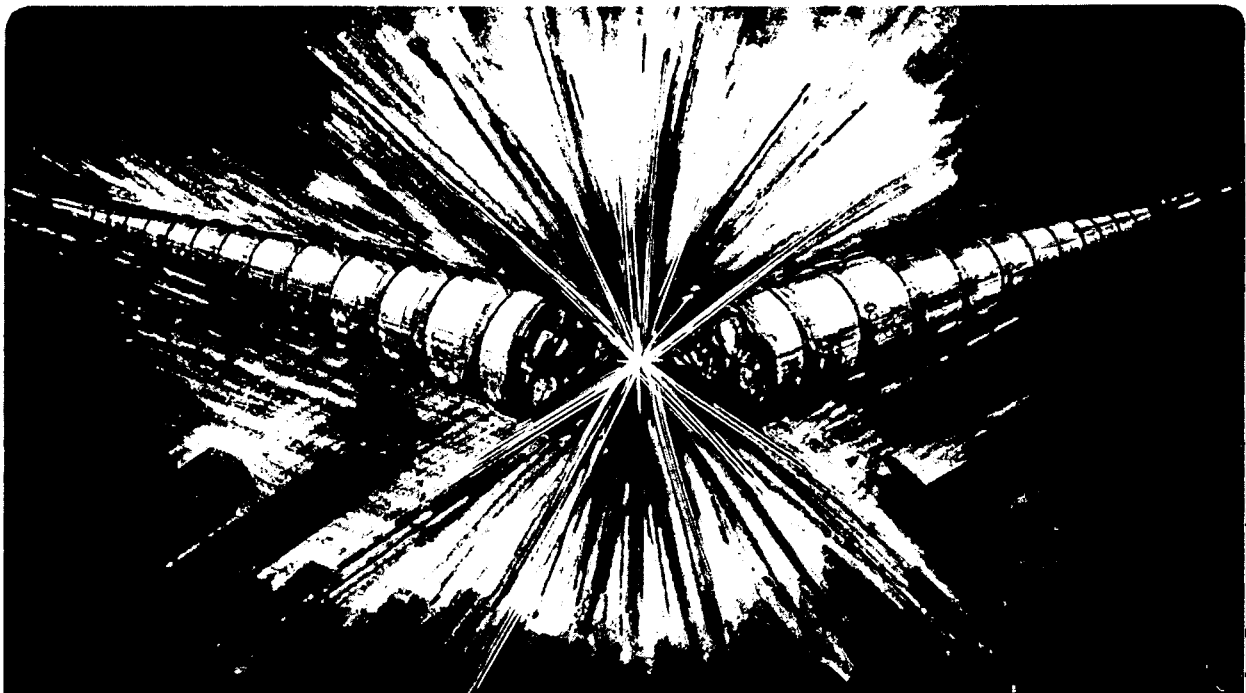
Accelerator & Fusion Research Division

Presented at the Second International Conference on Computer Simulation of Radiation Effects in Solids, Santa Barbara, CA, July 25-29, 1994, and to be published in Nuclear Instruments and Methods in Physics Research B

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July 1994



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LBL-35679
UC-426

Submitted to
2nd International Conference on Computer Simulation of Radiation Effects in Solids,
Santa Barbara, California
July 25-29, 1994

**Increasing the Retained Dose by
Plasma Immersion Ion Implantation and Deposition**

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July 22, 1994

This work was supported by the Electric Power Research Institute under Contract RP 8042-03, and the U.S. Department of Energy, Division of Advanced Energy Projects, under Contract No. DE-AC03-76SF00098.

Increasing the Retained Dose by Plasma Immersion Ion Implantation and Deposition

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Abstract

The retained dose of ions can be increased by Plasma Immersion Ion Implantation and Deposition (PIIID). A substrate is immersed in a metal or carbon plasma and a negative repetitively pulsed bias voltage is applied. During the pulses, an electric sheath is formed around the substrate and ions are accelerated through the sheath and implanted into the substrate. Direct and recoil ion implantation and sputtering take place during the pulses whereas low-energy deposition occurs between the pulses. The condensable plasma can be produced using a cathodic arc plasma source combined with a magnetic macroparticle filter. PIIID can be applied to perform fast high-dose implantations or to deposit thin films with broad intermixing at the film-substrate interface. The bias voltage duty cycle can be tuned to sputter away the film deposited during pulse off-time (similar to the method of sacrificial layer). We have simulated the PIIID process using the Monte Carlo code T-DYN 4.0. This code allows a calculation of the dose-dependent depth profile for a process with deposition and implantation phases, taking sputtering into account. Predicted retained doses and experimentally obtained retained doses measured by Rutherford backscattering spectrometry are compared.

Introduction

Plasma Immersion Ion Implantation (PIII) as a way of implanting gaseous ions into conducting substrates without using an ion beam source has been developed by Conrad and co-workers [1]. In this method, a substrate is immersed in a plasma and a negative repetitively pulsed bias voltage is applied to the substrate; an electrical sheath is formed around the substrate and ions are accelerated through the sheath and implanted into the substrate. We have applied this approach to plasmas of condensable materials such as metals or carbon. In this case, low-energy deposition occurs between the pulses whereas direct and recoil ion implantation and sputtering of the deposited film takes place during the pulses. The plasma is produced using a cathodic arc plasma source combined with a magnetic filter [2] to remove the micron-size solid or liquid particles which are produced by the cathode spot along with the plasma. This process is called Plasma Immersion Ion Implantation and Deposition (PIIID) [3, 4].

This materials modification process can be applied to perform fast high-dose implantations or to form thin films with a broad intermixing at the film-substrate interface. By varying the pulse bias voltage and duty cycle (ratio of pulse duration to pulse off-time), the depth profile of the implanted/deposited species can be varied over a wide range. By using a high pulse bias duty cycle it is possible to perform high-dose ion implantation without forming a film at the surface if the amount of material sputtered during the high voltage pulse is higher than or comparable to the amount of material deposited between the high voltage pulses. Also film properties such as mass density, internal stress, and film structure can be tailored within PIIID by changing the pulse bias regime, which determines the energy of the incident ions.

In the present paper we report on results of a comparison between predicted retained doses and experimentally obtained retained doses measured by Rutherford backscattering spectrometry.

Simulation of PIIID

It is desirable to be able to predict the depth profile for a given implantation-deposition process or to determine the process parameters in such a way that a given depth profile can be achieved. We have simulated the PIIID process using the Monte Carlo code T-DYN 4.0 [5]. This code allows a calculation of the dose-dependent depth profile for a process with simultaneous deposition and implantation taking sputtering into account.

The input parameters which determine the final depth profile are the chemical composition of the substrate and the plasma, the ion energy and the duty cycle D of the pulsed bias voltage given by the pulse duration τ_{pulse} and the pulse off-time τ_{off} as $D = \tau_{\text{pulse}} / (\tau_{\text{pulse}} + \tau_{\text{off}})$. As an example, the depth profile for a PIIID process of gold into/on silicon with an ion energy of 5 keV has been simulated for different pulsed bias duty cycles. For comparison, conventional ion implantation (corresponding to 100% duty cycle) with the same energy has been simulated too.

Figs. 1 and 2 show the result of the simulation for different duty cycles. For conventional ion implantation with a constant ion energy of 5 keV we observe a typical implantation depth profile reaching a sputter-limited saturation of retained dose of about $2 \times 10^{16} \text{ cm}^{-2}$ at an incident dose of $3 \times 10^{16} \text{ cm}^{-2}$ (Fig. 1). The maximum of the implanted species profile is at a depth of 6 to 10 nm depending on the dose (Fig. 2a). For a 50% duty cycle pulsed bias it is remarkable that the final depth profile is also sputter-limited and almost identical to the profile of conventional ion implantation (Fig. 2b), and so is the maximum retained dose (Fig. 1). This means that it is possible to create the same depth profile as obtained by conventional ion implantation but without using an ion beam source (except for low doses $< 10^{16} \text{ cm}^{-2}$ where we observe a slightly higher surface concentration). The result for a duty cycle of 20% is similar: There exists a sputter-limited final depth profile and a maximum of the implanted species at about 6 nm (Fig. 2c), but the retained dose is a factor of about two higher (Fig. 1). Thus it is possible to obtain depth

profiles which cannot be created in principal by conventional ion implantation! A further decrease of the pulsed bias duty cycle to 10% leads to the formation of a surface layer with a well intermixed interface. Fig. 2d shows the surface layer formation for 1% duty cycle, and in this case the retained dose is not limited and growth monotonically with the incident dose, but is materialized as a surface film.

The depth profiles as a function of the duty cycle for low and high doses are shown in Figs. 3 and 4, respectively. At a low dose of 10^{16} cm^{-2} (Fig. 3) the profiles are significantly different, whereas at higher doses (Fig. 4) the profiles are characterized by an almost constant percentage of the implanted species from the surface to a certain depth and a long intermixed tail. A remarkable feature is that a reduced duty cycle increases the maximum achievable concentration of the implanted species from the surface to the mean penetration depth.

From these simulations we can conclude that the bias duty cycle is a key parameter which determines the profile of the implanted/deposited species. The transition from a sputter-limited retained dose (high duty cycle) to film formation (low duty cycle) depends on both the substrate material and ion species, and we have shown it here for the example of gold implantation/deposition into/on silicon.

Comparison between Simulation and Experiment

To prove the reliability of the simulation for predicting experimental results, we have carried out a PIIID of gold in silicon with an ion energy of 4 keV and different duty cycles. The arc current for operating the vacuum arc plasma source was 200 A, the arc duration 5 ms and the arc repetition rate 1 s^{-1} . The silicon substrate was immersed into the gold plasma and a pulsed bias voltage of - 2kV was applied to the substrate during the plasma exposure. The bias pulse duration was 2 μs and the pulse off-time 2 μs for 50% duty cycle, 15 μs for 12% duty cycle, and no bias was applied for 0% duty cycle. Since the

mean ion charge state in a vacuum arc produced gold plasma is 2 [4], the mean ion energy during the high voltage pulses is 4 keV. All samples were deposited under identical conditions except the bias duty cycle of the substrate. It was assumed that the incident dose and retained dose for the sample deposited without bias voltage are identical. The retained dose for this sample was $3 \times 10^{17} \text{ cm}^{-2}$ determined by Rutherford backscattering spectrometry (RBS). The gold ions of a vacuum arc plasma have a directed velocity of about 10^4 m/s [5] which corresponds to a kinetic energy of 100 eV. The sputter yield for such a low ion energy is only 1% (determined by T-DYN 4.0), which supports the assumption that the RBS determined retained dose is equal to the incident dose. Table 1 shows that the total retained doses determined by a T-DYN 4.0 simulation for bias duty cycles of 50% and 12% agree fairly well with the experimentally determined retained doses obtained by RBS. The depth resolution of RBS of about 5 nm does not allow a comparison of the simulated and measured depth profiles, but RBS gives relatively accurate values for the absolute amount of the implanted species in the substrate and confirms the simulated data well. The retained doses are approximately one order of magnitude less than the incident doses indicating that indeed a sputter limited saturation of the retained dose can be reached for a PIIID process, but the value of the maximum retained dose can be tailored by varying the pulse bias duty cycle which is not possible for a conventional implantation.

Conclusions

Plasma Immersion Ion Implantation and Deposition provides a very versatile means of modifying surfaces of materials. The surface properties can be tailored over a wide range by adjusting the process parameters such as pulsed bias voltage and bias duty cycle. Implantation depth profiles which are usually obtained using a conventional ion implanter can be created without using an ion beam source. Since the process combines deposition and implantation (including sputtering), it is possible to increase the sputter limited

maximum retained dose of a conventional ion implantation by counteracting the sputtering effect during the high voltage pulses by deposition between the pulses (similar to the method of sacrificial layer [6]). The method is very efficient; typical implantation/deposition rates are $10^{15} \text{ cm}^{-2}\text{s}^{-1}$ in the time average and $10^{17} \text{ cm}^{-2}\text{s}^{-1}$ during the plasma pulse.

The numerical simulation of the process using the Monte Carlo code T-DYN 4.0 provides a reliable prediction of the retained dose and is a convenient means to determine the necessary process parameters to obtain a desired retained dose.

Acknowledgments

This work was supported by the Electric Power Research Institute under Contract RP 8042-03, and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Advanced Energy Projects, under Contract No. DE-AC03-76SF00098.

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Tables

Table 1: Comparison of retained doses for the PIIID process of gold into silicon obtained by T-DYN 4.0 simulation and Rutherford backscattering spectrometry.

Ion energy (eV)	pulse bias duty cycle	Incident dose (in 10^{16} cm^{-2})	Retained dose obtained by T-DYN 4.0 (in 10^{16} cm^{-2})	Retained dose obtained by RBS (in 10^{16} cm^{-2})
4 keV	50%	30	1.78	1.84
4 keV	12%	30	4.40	4.17

Figure Captions

Fig. 1: Retained dose as a function of incident dose for PIIID of gold into silicon, ion energy 5 keV, for different duty cycles. Simulation using T-DYN 4.0.

Fig. 2: Atomic fraction of gold in silicon as a function of depth for different incident doses, ion energy 5 keV. (a) duty cycle 100% (conventional implantation), (b) duty cycle 50% (PIIID), (c) duty cycle 20% (PIIID), (d) duty cycle 1% (PIIID). Simulation using T-DYN 4.0.

Fig. 3: Atomic fraction of gold in silicon as a function of depth for different duty cycles, ion energy 5 keV, incident dose 10^{16} cm⁻². Simulation using T-DYN 4.0.

Fig. 4: Atomic fraction of gold in silicon as a function of depth for different duty cycles, ion energy 5 keV, incident dose 10^{17} cm⁻². Simulation using T-DYN 4.0.

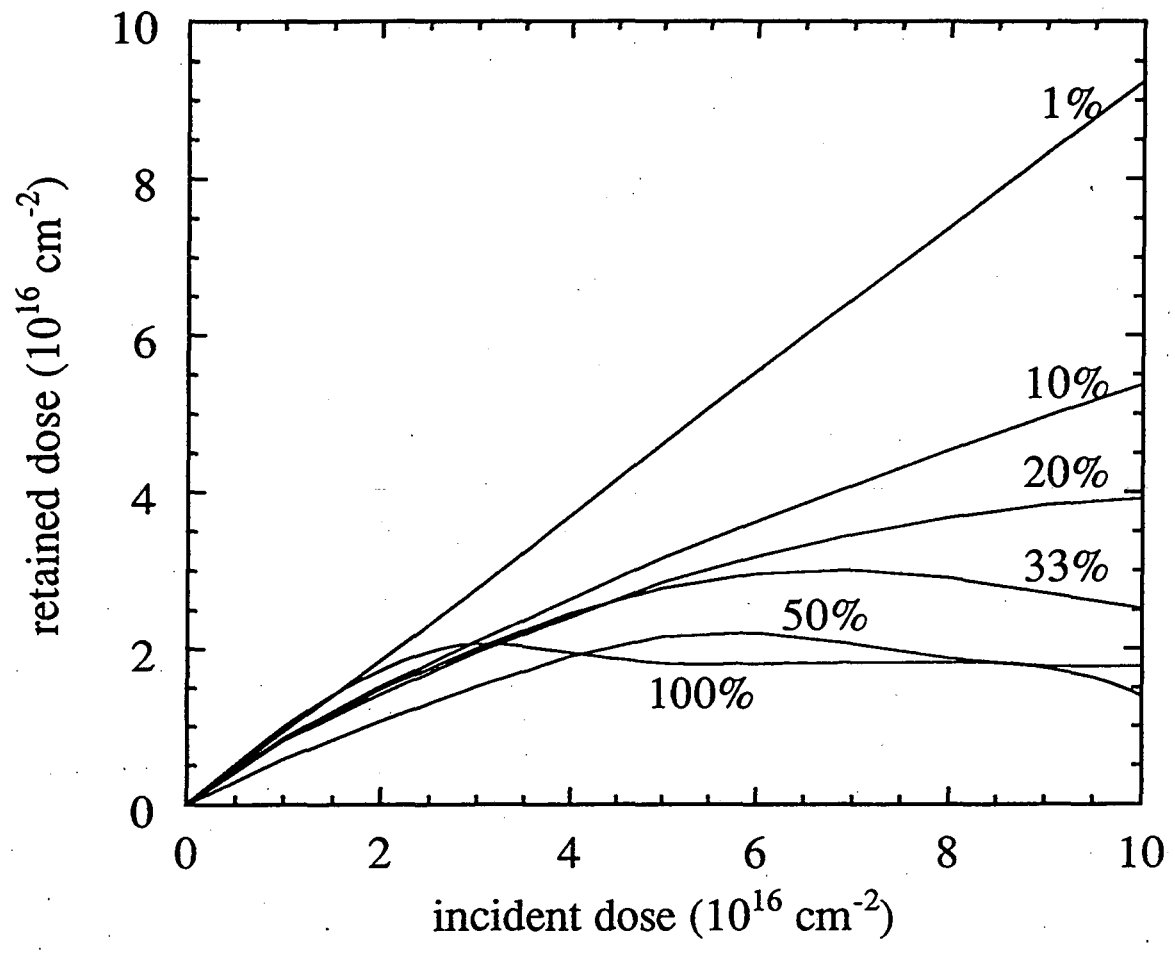


Figure 1

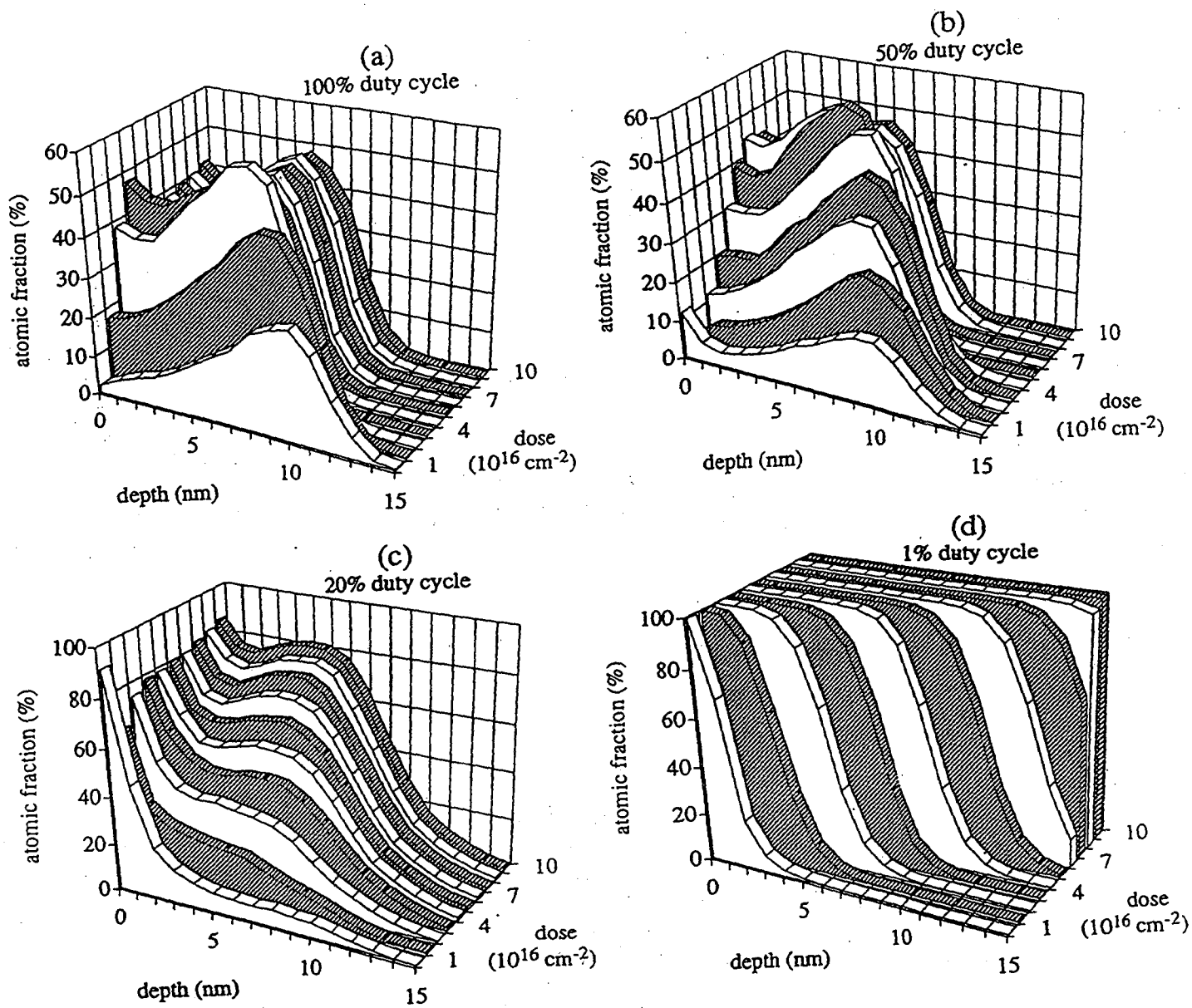


Figure 2

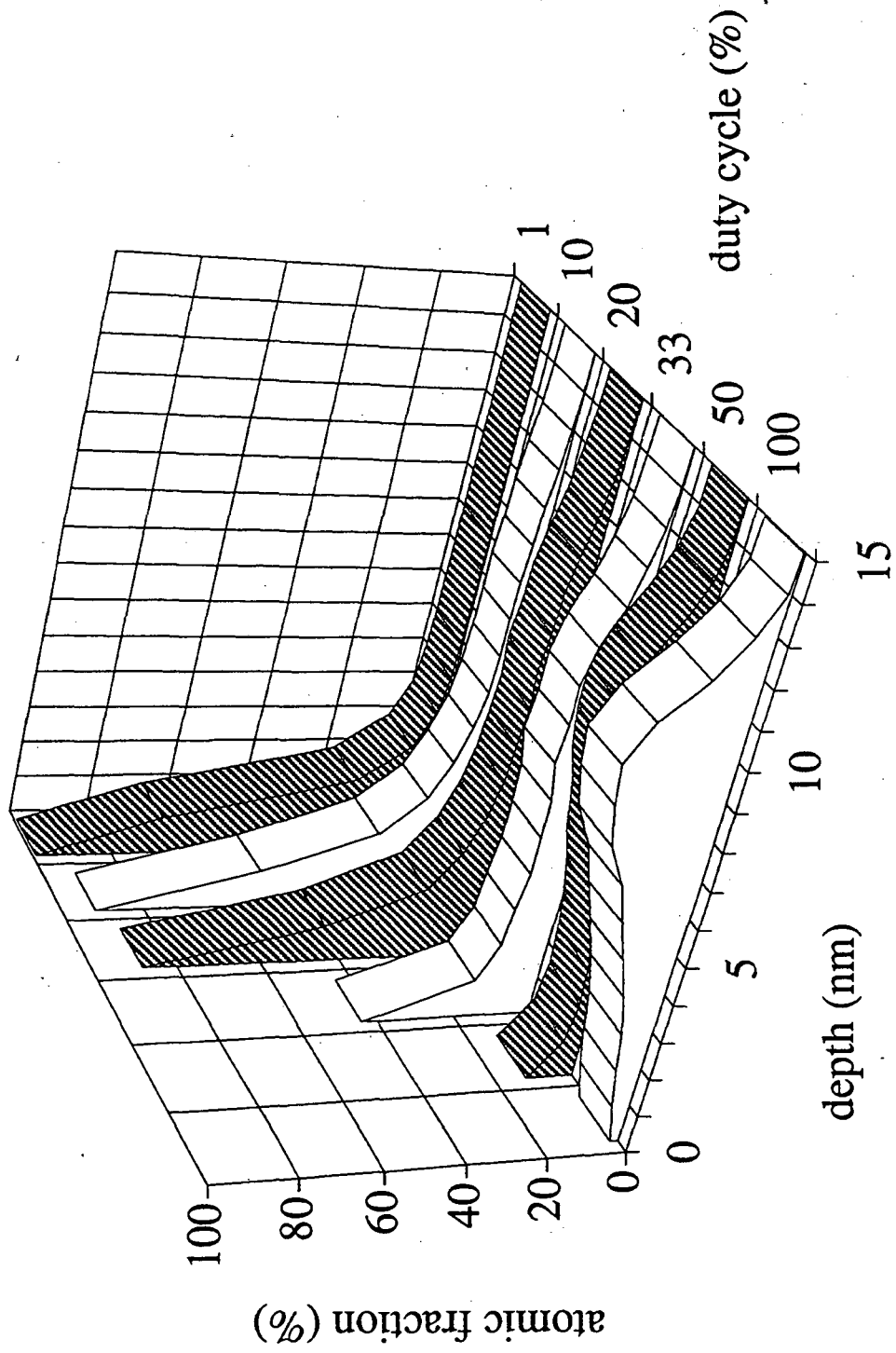


Figure 3

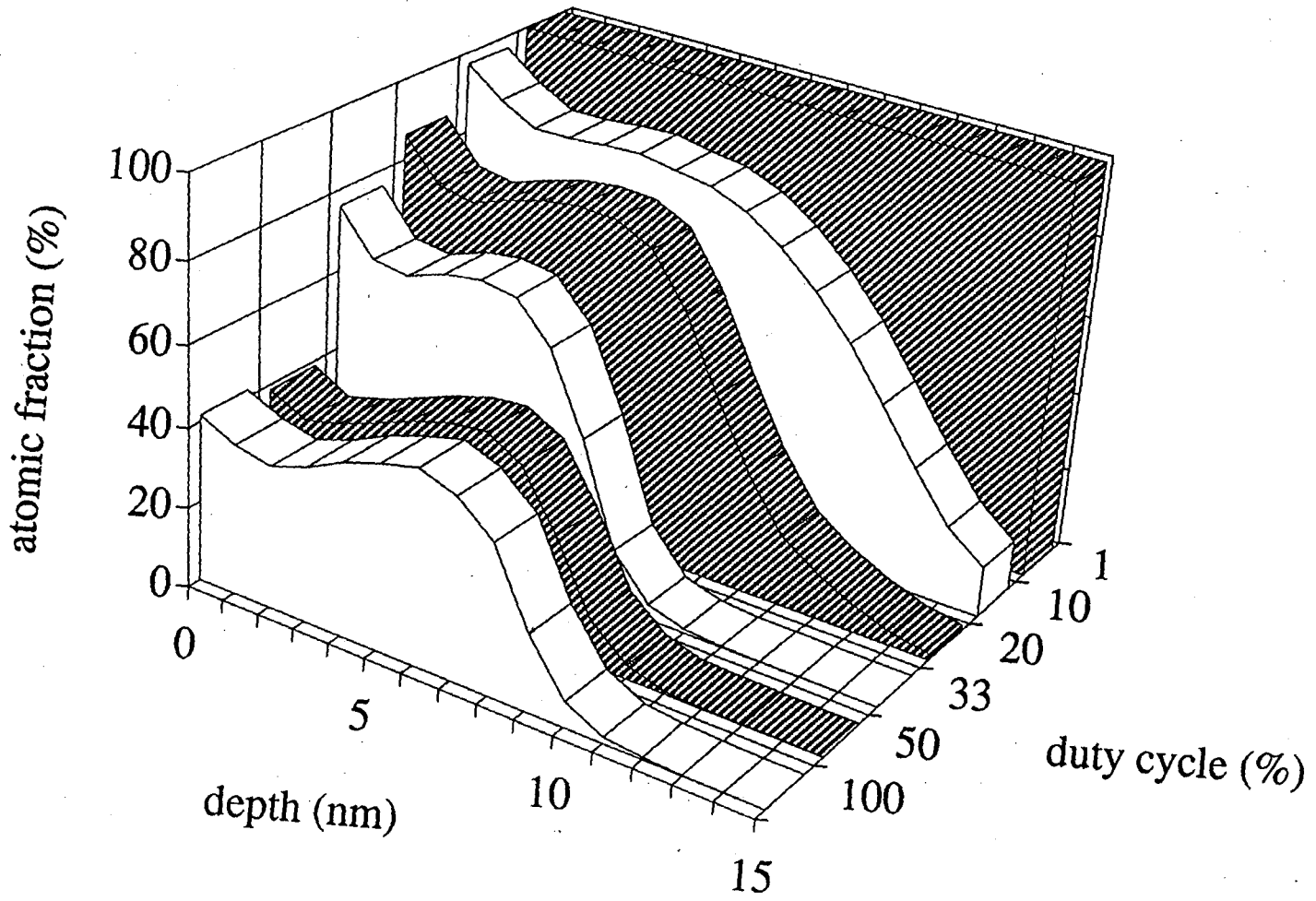


Figure 4

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