CONF-950220--10

LBL-36783
UC-426

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Accelerator & Fusion Research Division

Presented at the Ninth International Conference on
Ion Beam Modification of Materials, Canberra, Australia,
February 5–10, 1995, and to be published in the Proceedings

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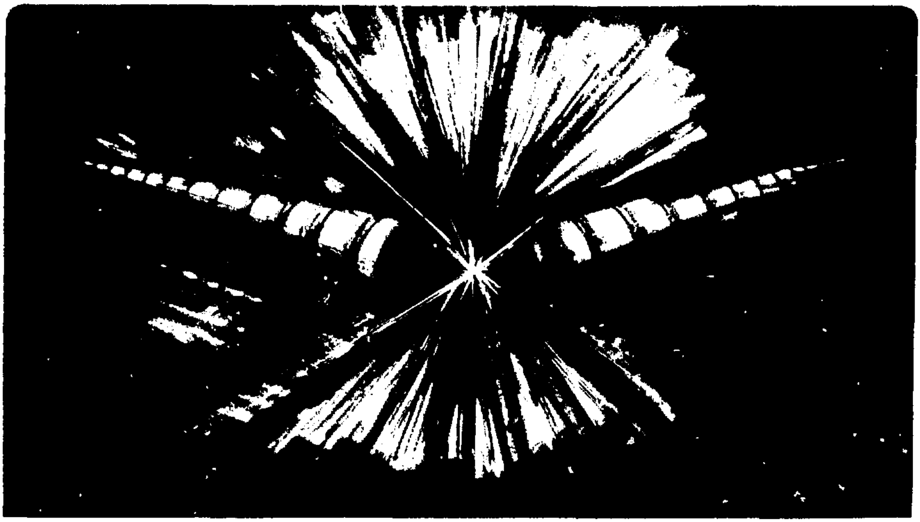

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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

IN-SITU DEPOSITION OF SACRIFICIAL LAYERS DURING ION IMPLANTATION

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ABSTRACT

The retained dose of implanted ions is limited by sputtering. It is known that a sacrificial layer deposited prior to ion implantation can lead to an enhanced retained dose. However, a higher ion energy is required to obtain a similar implantation depth due to the stopping of ions in the sacrificial layer. It is desirable to have a sacrificial layer of only a few monolayers thickness which can be renewed after it has been sputtered away. We explain the concept and describe two examples: (i) metal ion implantation using simultaneously a vacuum arc ion source and filtered vacuum arc plasma sources, and (ii) Metal Plasma Immersion Ion Implantation and Deposition (MePIIID). In MePIIID, the target is immersed in a metal or carbon plasma and a negative, repetitively pulsed bias voltage is applied. Ions are implanted when the bias is applied while the sacrificial layer suffers sputtering. Low-energy thin film deposition - repair of the sacrificial layer - occurs between bias pulses. No foreign atoms are incorporated into the target since the sacrificial film is made of the same ion species as used in the implantation phase.

I. INTRODUCTION

Ion implantation is a well-established method to modify the near-surface properties of materials, and a wide range of applications exists. A unique feature of ion implantation is that the fraction of implanted species in the target material can exceed the limits given by (equilibrium) thermodynamics. However, the retained dose of implanted ions is limited by sputtering: a significant fraction of ions is removed from the target by sputtering when the dose is high.

Clapham and coworkers [1] used a thin carbon coating ("sacrificial layer") of the target to increase the retained dose of iridium ions implanted into copper. Carbon was chosen because its sputtering rate is relatively small due to its small atomic density and nuclear stopping power. It was shown that the iridium concentration could be significantly enhanced. The sacrificial layer was deposited prior to ion implantation. Its thickness had to be carefully chosen: if it is too thin then it will be sputtered away before the implantation is finished, and if it is too thick then the incident ions stop in the layer rather than in the underlying target. Another drawback is ion mixing of carbon with the target, which may not be tolerable in some applications.

In ion beam assisted deposition (IBAD), thin films are formed while bombarded with ions. This results in improved film quality and adhesion. The energy of ions is usually too low to speak of ion implantation. Russian scientists have recently reported about vacuum arc metal ion sources which can operate alternately in an ion deposition and ion implantation mode by switching the ion extraction voltage [2, 3]. This suggests that sacrificial layers can be deposited not only prior but during ion implantation.

In this paper, we investigate conditions for *in-situ* deposition of sacrificial layers. Two experimental approaches to the problem are considered: (i) metal ion beam implantation with simultaneous pulsed plasma deposition, and (ii) metal plasma immersion ion implantation and deposition with matched bias duty cycle.

II. IN-SITU DEPOSITION OF A SACRIFICIAL LAYER: CONCEPT

The retained dose is limited by sputtering since not only the original target but also previously implanted ions are sputtered. The maximum achievable concentration of implanted ions is reached when the amount of implanted ions leaving the surface by sputtering equals the amount of incident ions. It is useful to distinguish between the partial sputtering rates of implanted material and original target material, $\gamma_i = \Delta N_i / N_i$ and $\gamma_t = \Delta N_t / N_i$, respectively; where ΔN_i is the number of sputtered atoms of previously implanted material, N_t is the number of sputtered target atoms, and N_i is the number of incident ions (all numbers are counted for a given period of time). Both γ_i and γ_t depend on the energy of incident ions, the angle of incidence, the actual target composition, and other parameters. The ratio between the partial sputtering rates is mainly determined by the fraction α of the implanted material at the surface, $0 \le \alpha \le 1$. The more α increases the more implanted material is sputtered.

The idea of a "sacrificial layer" is to protect the original surface of the target by a very thin coating. Sputtering is not avoided, but it is the sacrificial layer that is sputtered. Sputtered atoms are lost from the very top atomic monolayers, and thus the sacrificial layer could be kept very thin (a few monolayers) if a "repair" is possible during ion implantation. Such a "repair" is possible by *in-situ* deposition of a thin film, preferably of the same material as implanted since this does not introduce foreign species. Of course, other materials have been used when implanting gaseous ions.

In the following we assume that a thin film is deposited of the same material as is implanted. The partial sputtering rate of the implanted material is the partial sputter rate of the implanted *and* deposited material (the index "i" which refers to both the implanted and deposited material), $\gamma_i^{imp} = \Delta N_i^{imp} / N_i$ and $\gamma_i^{dep} = \Delta N_i^{dep} / N_i$ with $\gamma_i = \gamma_i^{imp} + \gamma_i^{dep}$. The loss of implanted ions can be minimized at the expense of the loss of deposited ions. In this way, very high concentrations of implanted ions are possible. Ion beam mixing of deposited ions with target material occurs, and a two peak implantation profile can be observed: the deep peak results from the stopping of implanted ions, and the one close to the surface comes from knock-on collisions occurring in the deposited sacrificial film. The difficulty for specific implantation systems is to determine the ratio of deposited and implanted material in order to maintain the sacrificial layer without growing a thick film. In the next sections we consider two examples.

III. DEEP ION IMPLANTATION USING A VACUUM ARC METAL ION SOURCE WITH SIMULTANEOUS METAL PLASMA DEPOSITION

Large area metal ion implantation is conventionally done using a broad beam metal ion source such as a vacuum arc ion source (see [4] and references therein). Ions of the cathode material are produced in vacuum arc cathode spots. They are extracted from the plasma to form an ion beam by an extractor system which consist commonly of a three-grid accel-decel system. The ion energy equals the extractor voltage times the ion charge (which is material dependent and typically 2 or 3, Ref. [4]), and energies up to 300 keV are frequently used. Since this is much more than the energy achieved in plasma immersion ion implantation (see next section), we refer to these implantation as "deep" implantations (the higher the energy the deeper the implantation).

In-situ plasma deposition of a sacrificial layer can be done either using the ion source itself, but with the extraction voltage switched off, as a source of flowing, low-energy metal plasma [2, 3], or, for instance, a separate filtered vacuum arc metal plasma source [5] can be used as shown in Fig. 1. "Filtered" refers here to the removal of micron-size "macroparticles" which are usually produced in vacuum arc cathode spots. Several of such plasma sources could be used for large area, homogeneous deposition when the ion beam cross section is large. To avoid incorporation of foreign species, the cathodes of the ion beam source and the plasma sources should be made from the same material. In some cases, however, it could be desirable to deposit the material of the original target or something else determined by the application.

IV. SHALLOW ION IMPLANTATION USING METAL PLASMA IMMERSION ION IMPLANTATION AND DEPOSITION

Conrad and co-workers [6] invented another approach to gaseous ion implantation, called Plasma Source Ion Implantation (PSII) or Plasma Immersion Ion Implantation (PIII). The idea is to immerse the substrate (target) in a gaseous plasma, and repetitively bias it to a high negative potential. This leads to a repetitive formation of an electric sheath surrounding the substrate through which the plasma ions are accelerated toward the substrate and implanted below its surface. The technique has recently been expanded to metal plasmas [7, 8] providing a new method of plasma surface processing due to the condensable nature of metal plasmas. This Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) technique [8] includes both ion implantation and deposition, correlated to the presence and absence of the high negative bias potential, respectively (Fig. 2). Because high voltage pulsers with high duty cycle are inefficient (no secondary electron supression) and expensive, MePIIID is more suited to lower energy and thus to relatively shallow implantation compared to implantation using vacuum arc ion sources.

MePIIID offers an elegant new way of doing *in-situ* deposition of sacrificial layers. A thin film (sacrificial layer) is deposited in the absence of bias; this film suffers sputtering when the target is biased, followed by low-energy thin film deposition, etc. In this way, the sacrificial layer is repetitively "repaired". Note that no foreign atoms are incorporated into the substrate since the sacrificial layer is made of the same ion species as used in implantation. Deposition and sputtering have to be balanced to obtain a sustainable repair. This can be done by operating at a suitable bias duty cycle which can be defined as

$$\delta = \tau_p / (\tau_p + \tau_0) \qquad (1)$$

where τ_p is the duration of individual bias pulses and τ_0 is the time between two pulses. If the duty cycle is too low, a metal (or carbon) film grows on the target; if the duty cycle is too high, the target including the previously implanted ions will be sputtered. The balance equation can be written as follows

$$\left(J_i\,\xi_i + J_n\,\xi_n\right)\tau_0 = \left(\gamma_i\,J_i + \alpha\,p\,J_i - J_n\,\xi_n\right)\tau_p \qquad (2)$$

where J_i and J_n are the ion and neutral particle flux density incident the target, respectively, ξ_i and ξ_n are the ion and neutral sticking coefficient, γ_i is the actual material and ion-energy-dependent partial sputter rate of previously deposited and implanted ions ("actual" refers to the rate during a pulse), and p is a function proportional to the probability at which a deposited metal ion suffers a knock-on collision (recoil implantation). Some simplifying assumptions have been made in the derivation of equ. (2): (i) the incident flux is independent of the bias pulse duration, and (ii) the term "pulse duration" is well-defined, assuming short bias rise and fall times. Equ. (2) can be further simplified since we use vacuum arc metal plasmas which are fully ionized, thus $J_n = 0$. Then, equ. (2) can be approximated by

$$\delta = \left(\gamma_i + 1\right)^{-1} \qquad (3)$$

This equations gives a rough estimate of the bias duty cycle that should be used to obtain a maintained repair of the sacrificial layer.

Since there is no sacrificial layer at the beginning of the process, sputtering starts with target material only. This suggests operating at a variable duty cycle: A protective film should be deposited at the beginning of the process, i.e. the bias duty cycle should be zero until a film has been formed, the thickness of which must be thick enough to cover the target but thin enough that energetic ions can be implanted through the film.

Once the protective film is formed, bias pulses can be applied to begin the implantation. The duty cycle of the implantation-deposition process can be matched to rebuild the sputtered film after each implantation pulse. In addition to direct implantation, recoil implantation will occur, leading to a relatively broad intermixed layer. This layer is very beneficial when a well-bonded film is desired. If no film is required, it can be at least partially removed at the end of the implantation process simply by enhancing the duty cycle. Another way is to fill the vacuum chamber with a gas like argon and remove the metal film by argon sputtering using the same bias pulse system.

V. MONTE CARLO SIMULATION

We used the Monte Carlo simulation program T-DYN version 4.0 (Ref. [9]) which is a dynamic version of the better-known standard cascade TRIM code [10]. In contrast to TRIM, the code T-DYN takes into account gradual dynamic changes of the target (= substrate) such as composition and thickness alterations during ion beam bombardment or film growth.

The two techniques of ion beam implantation with *in-situ* deposition and MePIIID can be simultaneously investigated using the T-DYN code. In ion beam implantation, the ratio of implanted dose to deposited dose is associated with the number of ion beam pulses per ion deposition pulse. Calibration can be done for a given geometry, ion beam current, arc current, and pulse length. Alternatively, tuning of the implantation-deposition ratio can be done by changing other parameters such as the ratio of ion beam pulse length to plasma deposition pulse length. In MePIIID, the implantation-deposition ratio is simply determined by the bias duty cycle, and we use this parameter in the simulation.

As an example, we studied the implantation of tungsten ions into silicon. The total dose (including deposition) was in the range 5×10^{16} to 2×10^{17} ions / cm^2. The ion energy was 75 keV in the implantation phase, corresponding to an ion extraction voltage (ion beam implantation) or bias voltage (MePIIID) of 25 kV (mean ion charge state of vacuum-arc-produced tungsten is 3+). Figure 3 shows the tungsten depth profile for various bias duty cycles at a constant dose of 2×10^{17} ions / cm^2. 100% duty cycle corresponds to pure ion implantation without deposition of a sacrificial layer. The retained dose of tungsten is clearly limited by sputtering. A smaller duty cycle (increasing deposition of sacrificial layer) leads to an increase of the retained dose. When the duty cycle becomes smaller than 10%, a layer starts to grow. Figure 4 shows implantation profiles for a constant duty cycle of 50% as a function of dose. The profile reaches its steady-state shape at a dose of 1.5×10^{17} ions / cm^2.

VI. SUMMARY

In-situ deposition of a sacrificial layer can lead to new, previously unattainable implantation profiles. The retained dose can be significantly greater than in conventional ion implantation. As an example, tungsten ion implantation into silicon has been simulated using the Monte Carlo code T-DYN. The data obtained can be interpreted, for example, (i) in terms of using simultaneously a vacuum arc ion source and a filtered vacuum arc plasma source, or (ii) in terms of the new technique of duty-cycle-matched MePIIID. Here, deposition between bias pulses is matched with sputtering during bias pulses . In both cases, direct and recoil ion implantation is obtained. No foreign atoms are incorporated into the target since the sacrificial layer is made of the same ion species as used for ion implantation.

ACKNOWLEDGMENTS

This work was supported by the Electric Power Research Institute under Award Number 8042-03 and the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract Number DE-AC03-76SF00098.

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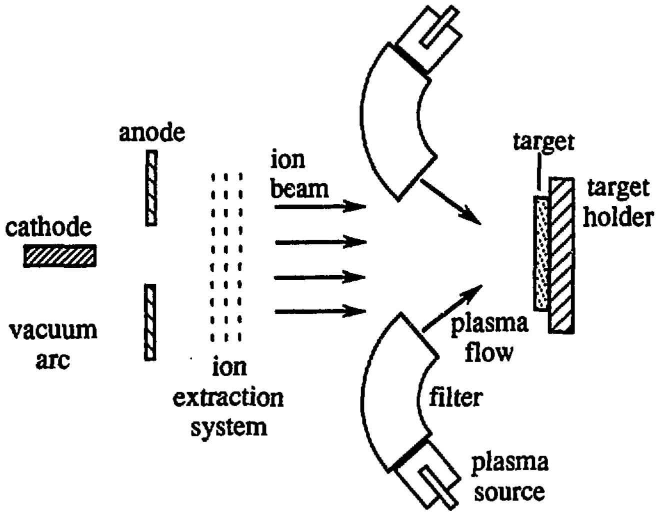
FIGURE CAPTIONS

Fig. 1 Schematic setup of *in-situ* deposition of sacrificial layers using filtered vacuum arc plasma sources while implantation is done using a vacuum arc ion source.

Fig. 2 Schematic setup of *in-situ* deposition of sacrificial layers using the MePIIID technique.

Fig. 3 Monte-Carlo simulation of tungsten ion implantation (75 keV, 2×10^{17} ions / cm^2) into silicon. The bias duty cycle corresponds to the number of energetic ions per deposited ions.

Fig. 4 Monte-Carlo simulation of tungsten ion implantation (75 keV, 50% duty cycle) into silicon as a function of dose.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ion
beam
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target
holder
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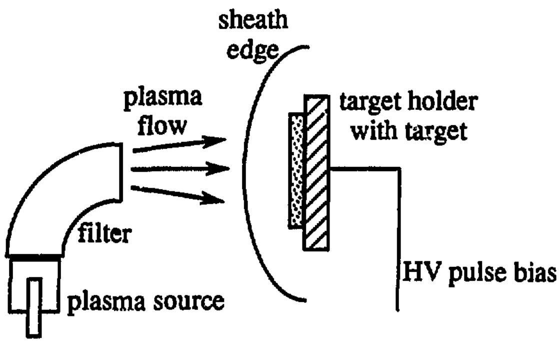
vacuum
arc
ion
extraction
system
plasma
flow
filter
plasma
source

Fig. 1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plasma
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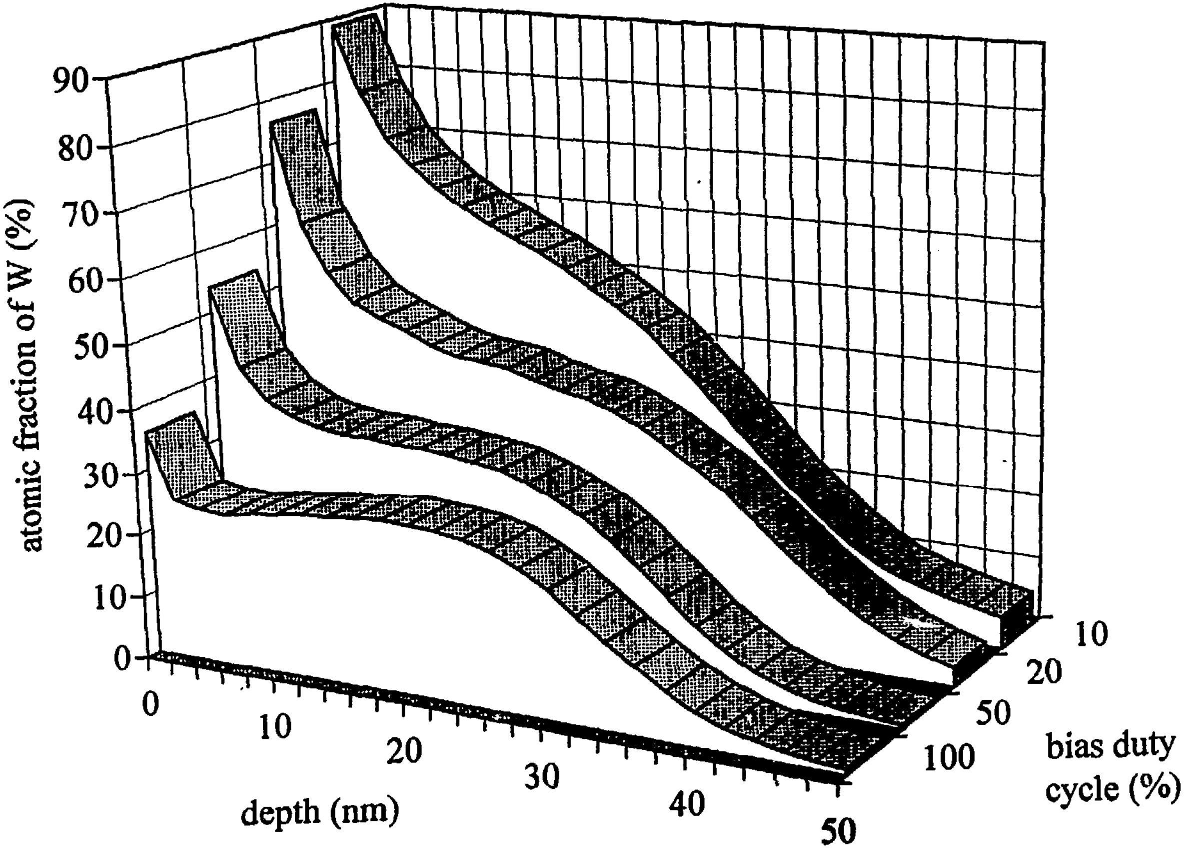
Fig. 2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80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
depth (nm)
10
20
50
100
bias duty
cycle (%)

Fig. 3

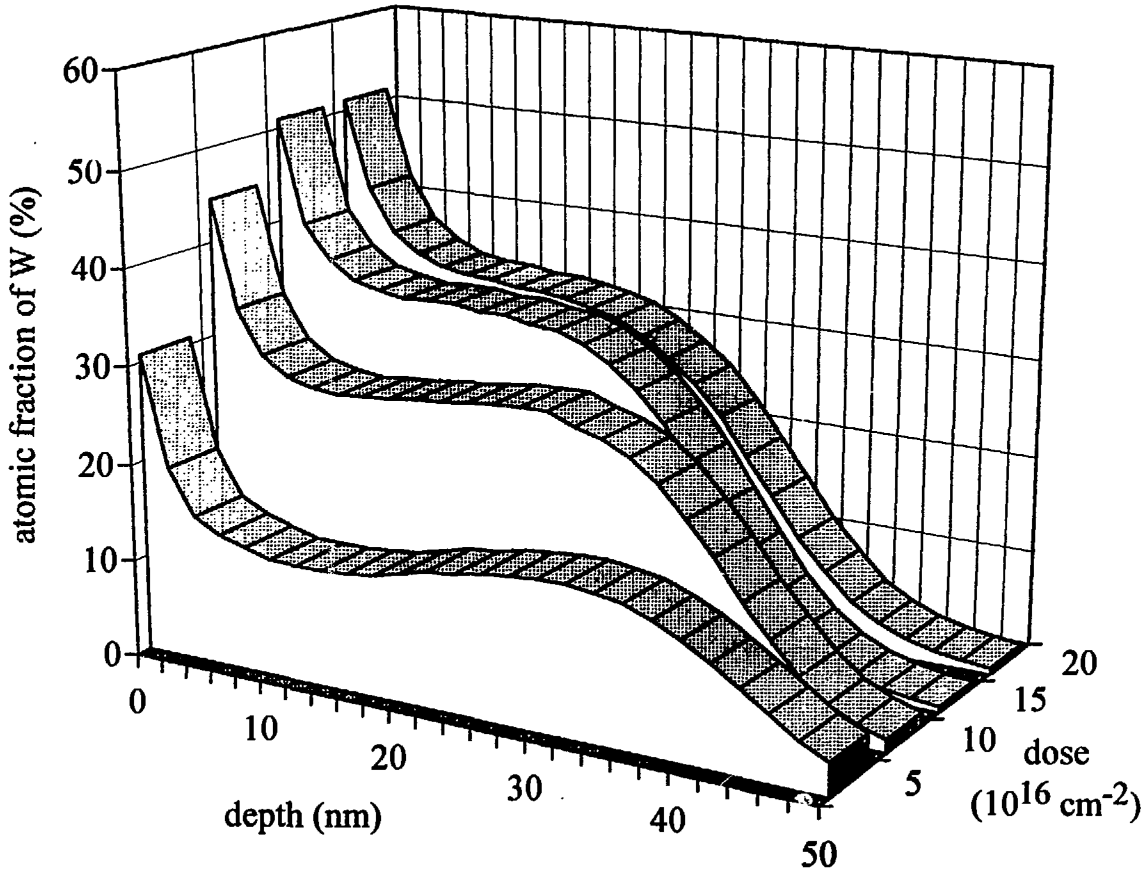
atomic fraction of W (%)
0
10
20
30
40
50
60
depth (nm)
0
10
20
30
40
50
dose
(10^{16} cm^{-2})
5
10
15
20

Fig. 4