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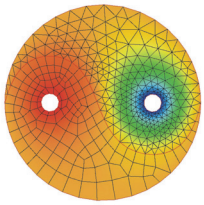
AKAPIT

COMPUTER METHODS IN MATERIALS SCIENCE

Informatyka w Technologii Materiałów

Vol. 9, 2009, No. 1



STRESS ANALYSIS OF SILICON-TITANIUM COATING CREATED BY ION BEAM SPUTTER DEPOSITION

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Abstract

The paper is devoted to the analysis of internal stresses generated in the silicon substrate during the ion beam sputter deposition (IBSD) which is used to produce a titanium coating and a material interface which is a mixture of Si and Ti and is denser than the original Si substrate. The stress in Si-Ti coating is difficult to measure but it can be evaluated by one of numerical methods. Much easier is to measure a variation of stress between interface layer and silicon part of coating by applying the Raman micro-spectroscopy.

The numerical model of IBSD can be split in two sub-models: the first one is for elastic collisions of substrate atoms with ion impinging into the substrate, and the second is for the generation of coating structure created.

Two programs: SRIM and TRIDYN, are used to this purpose. These programs are applied at the first stage of calculations based on binary collision approximation (BCA) with Monte Carlo (MC) algorithm and neglecting plastic effects. The energy loss for impinging ions appears because of their collisions with substrate atoms and appearance of a scattering angle for both particles. In each iteration of BCA the energy loss is evaluated. The density profile in respect of coating depth is calculated by using TRIDYN. On the basis of the density profile, the structure of coating can be determined from the Cerius^2 program by using models of molecular dynamics (MD). Following this, stress in the coating can also be evaluated. Macroscopic properties of Si-Ti sample are computed assuming that the energy of thermodynamic system is changing but the system volume is constant. Such thermodynamic system is known also as NVT particle ensemble. The coating process is controlled by parameters such as: beam current of sputtered atoms, temperature of a substrate, and time. It is assumed that the energy of sputtering beam is equal to15keV.

Key words: molecular dynamics, stress, IBSD, binary collision, coating

1. INTRODUCTION

The paper aims for

- Evaluation of stresses in Si-Ti coating,
- Prediction of mechanical properties of coatings,
- Proposition of growth model of coating.

In this paper a silicon-titanium bi-layer system is applied as the intermediate sub-layer.

Properties of such coating are strongly related to the microstructure and internal stresses that can be modify by introducing of intermediate sub-layer.

Numerical simulations are conducted for a model of a silicon-titanium system formed by applying one of ionic methods, e.g. the ion beam sputter deposition (IBSD) or the ion beam assisted deposition (IBAD). The numerical model of IBSD consists of two sub-models. The first one determines binary collisions, i.e. the Coulomb type collisions, and the second one, which is based on the molecular dynamics, is used for determination of molecular interactions. The density of atoms through a depth of a substrate is evaluated from the TRIDYN program.

ISSN 1641-8581

Stresses in coating structure are evaluated by using the Cerius^2 program.

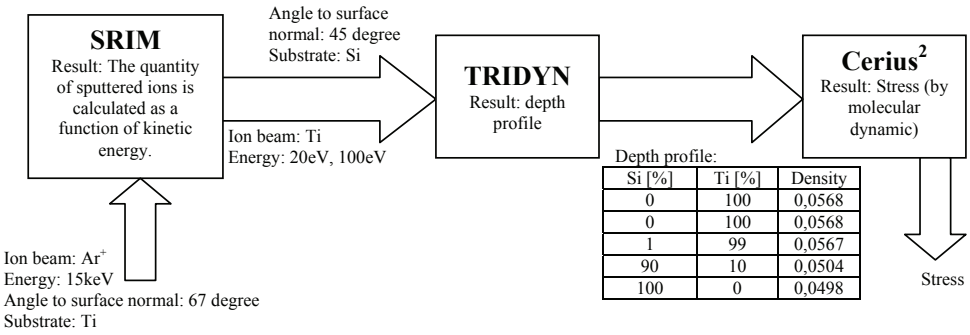

Fig. 1. *Block diagram of stress analysis.*

2. GENERAL DESCRIPTION OF SRIM AND TRIDYN PROGRAMS

The program TRIDYN [3], based on the Monte Carlo binary collision approximation (BCA) code of SRIM [9], is described in detail in [1,9]. Computations proceed according to the main program diagram shown in figure 2. The main loop is built for all projectiles. In the beginning of iteration, projectile parameters are set and a collision cascade is initiated. Next, trajectories of projectile and recoil atoms are calculated. Finally, at the end of iteration the relaxation of the structure, i.e. the dissipation of all kinetic energy, should be observed. General description of program flow is depicted in figure 2. More detailed information can be found in [1].

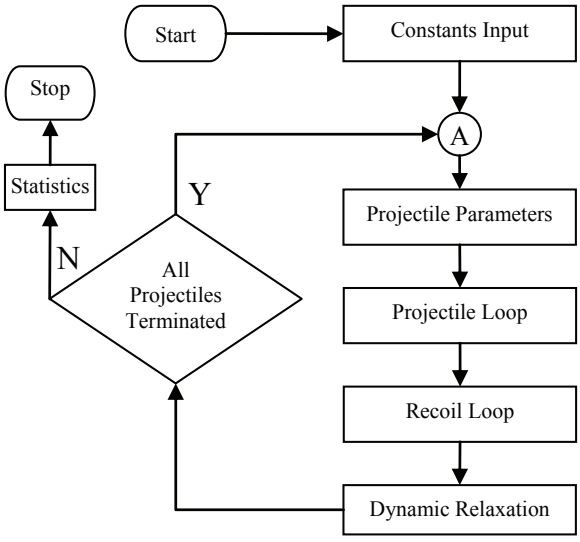

Fig. 2. *The flow chart of the TRIDYN algorithm [1].*

3. MATHEMATICAL MODEL OF ENERGY LOSS IN TRIDYN

The collision scattering angle, the elastic energy loss, local and nonlocal electronic energy losses are calculated for each projectile. The total energy loss is calculated as a sum of elastic and inelastic energy loss.

$$E_{total} = \Delta E_n + \Delta E_{el}\,. \quad (1)$$

Energy transferred during nuclear elastic collision is defined by

$$\Delta E_n = \gamma E \sin^2 \frac{\vartheta}{2} \quad (2)$$

where:

$$\gamma = \frac{4M_1M_2}{(M_1+M_2)^2} \quad (3)$$

and ϑ is the scattering angle computed by the 'magic formula' [5], where the universal two bodies' potential is used [9] as is proposed by Biersack [2].

The program TRIDYN is based on the model of binary collisions and the concept of an interatomic potential:

$$V(r) = \left(\frac{Z_1Z_2e^2}{r}\right)\phi\left(\frac{r}{a}\right), \quad (4)$$

where r is interatomic separation, e is the electronic charge, Z_1, Z_2 are atomic numbers of elements in collision, $\phi\left(\frac{r}{a}\right)$ is the screening function, and a is the screening length.

The screening function can be approximated by

$$\phi\left(\frac{r}{a}\right) = \sum_{i=1}^{n} C_i \exp\left(-d_i \frac{r}{a}\right), \qquad \sum_{i=1}^{n} C_i = \phi(0) = 1 \quad (5)$$

where C_i and d_i are constants chosen for the potential [1].

The screening length depends on Z_1 and Z_2 and can be written:

$$a = \frac{0.8853 a_0}{\left(Z_1^{\frac{1}{2}} + Z_2^{\frac{1}{2}} \right)^{\frac{2}{3}}}, \qquad (6)$$

where a_0 is the Bohr radius, Z_1, Z_2 are atomic numbers of elements in collision.

The inelastic nonlocal electronic energy loss (INEEL) is evaluated by the Linhard-Scharff formula. The local electronic energy loss (LEEL) can be determined by the Oen-Robinson formula. INEEL is independent of the impact parameter [1,2] and is defined by

$$\Delta E_{LS} = L_m N S_L(E), \qquad (7)$$

where S_L is the Linhard-Scharff stopping cross-section, L_m is a distance covered by a particle between collisions, and N is a target density.

where E is energy and the parameter k_L is defined by

$$k_L = \frac{1.212 (eV)^{\frac{1}{2}} \text{Å}^2 Z_1^{\frac{7}{6}} Z_2}{\left(Z_1^{\frac{2}{3}} + Z_2^{\frac{2}{3}} \right)^{\frac{3}{2}} M_1^{\frac{1}{2}}} \qquad (9)$$

with M_1 as an atomic mass of the first element, Z_1 as an atomic number of the first element, and Z_2 as an atomic number of the second element.

LEEL is related to the distance of closest approach in the atomic collisions [1,2] and is defined by

$$\Delta E_{OR} = \frac{0.045 \exp\left(-0.3 \frac{r_0}{a} \right)}{\pi a^2} S_L, \qquad (10)$$

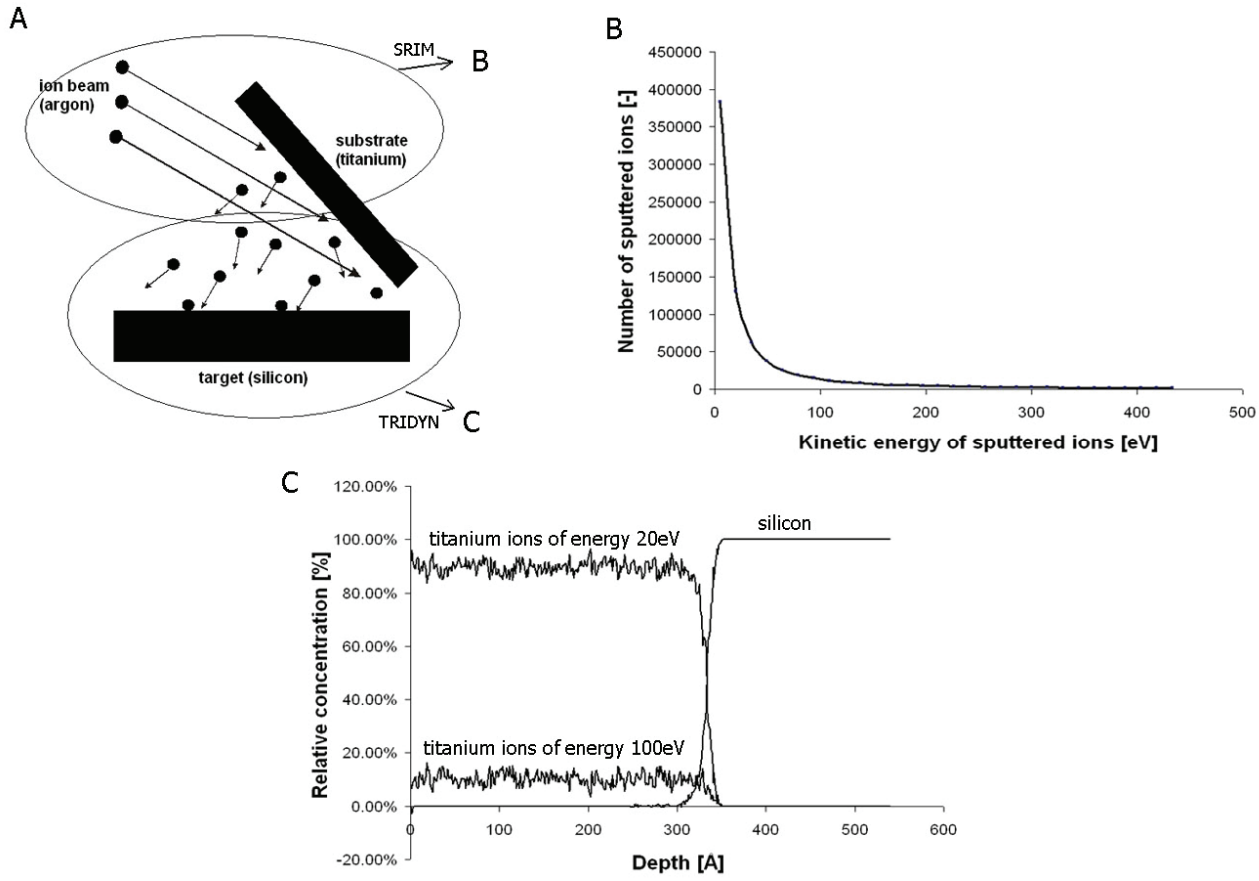

Fig. 3. *The scheme of IBSD process (A) and results from SRIM (B) and TRIDYN (C) programs.*

The Linhard-Scharff stopping cross-section is expressed by

$$S_L = k_L E^{\frac{1}{2}}, \qquad (8)$$

where r_0 is the apsis of trajectory which depends on the impact parameter p and energy E, a is the screening length, S_L is the Linhard-Scharff stopping cross-section.

4. QUANTITY OF IONS AND DENSITY PROFILE EVALUATION IN SRIM AND TRIDYN

First part of calculations is conducted by the SRIM program which solves the problem, where the argon ion beam of energy 15keV impinges on titanium substrate at angle of 67^0 to the surface normal. The quantity of sputtered ions is calculated as a function of kinetic energy. The next part of calculations is performed by using the TRIDYN program where a density profile of Si-Ti coating is evaluated. Sputtered ions have various energies. The problem is solved for two values of kinetic energy: 20eV and 100eV, and for a beam impinging at 45 degrees to Si substrate. The resulting thickness of produced coating is 540Å.

The IBSD process scheme is shown (part A) of figure 3 together with corresponding results (parts B and C). Quantity of sputtered ions is drawn against kinetic energy (part B) and the density profile of coating through the depth is shown part C.

5. METHOD OF STRESS CALCULATIONS IN CERIUS[2]

Calculations in the second stage of problem solution are conducted according to the diagram depicted in figure 5.

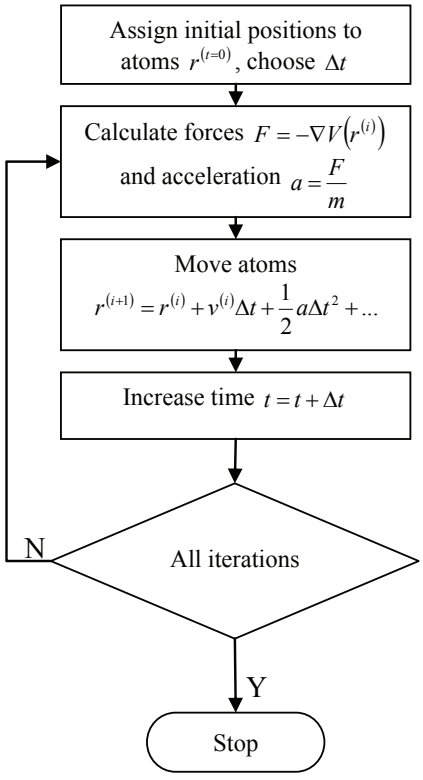

Fig. 4. *General algorithm for simulation of molecular dynamics [4].*

Firstly, the virtual structure of coating defined by a concentration of atoms in relation to depth and the initial configuration of particles is generated with help of TCL script in Cerius[2]. Force interactions between particles, trajectories of particle motion and the final configuration of particles in a coating are evaluated for such virtual structure. Trajectories of atoms result following integration of the Newton equation of motion. Force interactions between atoms are evaluated by using the concept of the universal force field (UFF) [4]. The new configuration of particles becomes more realistic and for this structure a stresses field is calculated.

6. STRESS MEASUREMENTS

The confocal dispersion Raman micro spectroscopy is used to measure variations of internal stresses between a substrate and an intermediate layer called also the interface. A substrate is the silicon target on which a titanium thin layer is deposited by using IBSD method.

The variation of stress is evaluated on the basis of Raman spectrum focusing initially a laser beam in a substrate and secondly the focus is situated in the interface area. The length of the applied laser beam is 532 nm and its power is 50 mV.

The shift of the silicon pick denoted as $\Delta\omega$ is measured along the vertical axis and is evaluated as the difference between the pick's position in figure 7(A) and the pick's position in figure 7(B). This shift is the data for calculation of the variation of internal stress σ between the intermediate layer and the silicon substrate. The relation [7,8] between $\Delta\omega$ and σ is given by the formula

$$\sigma(MPa) \approx -C_{Si} \times \Delta\omega(cm^{-1}) \qquad (11)$$

where C_{Si} is a parameter which can assume one of two values: 434 or 518.

7. RESULTS

7.1. Numerical results

The gradient density profile of coating is shown in figure 5a, and the ratio of titanium to silicon through a coating and substrate thickness is shown in figure 5b.

Stresses evaluated by Cerius[2] along the main three axes by using the molecular dynamic are presented in figure 6 for various temperatures.

substrate. Stress intensity is approximately equal to 5 GPa and oscillates around a linear function $y = -4 \times 10^{-5} x + 5.0986$. The particle concentration and stress decreases going deeper under surface of the substrate.

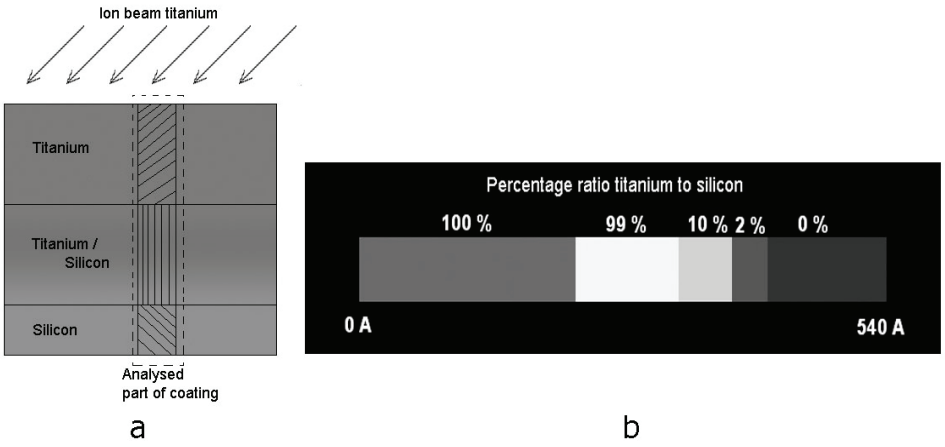

Fig. 5. *The gradient of density profile in Si-Ti coating (a) and the ratio of titanium in silicon (b).*

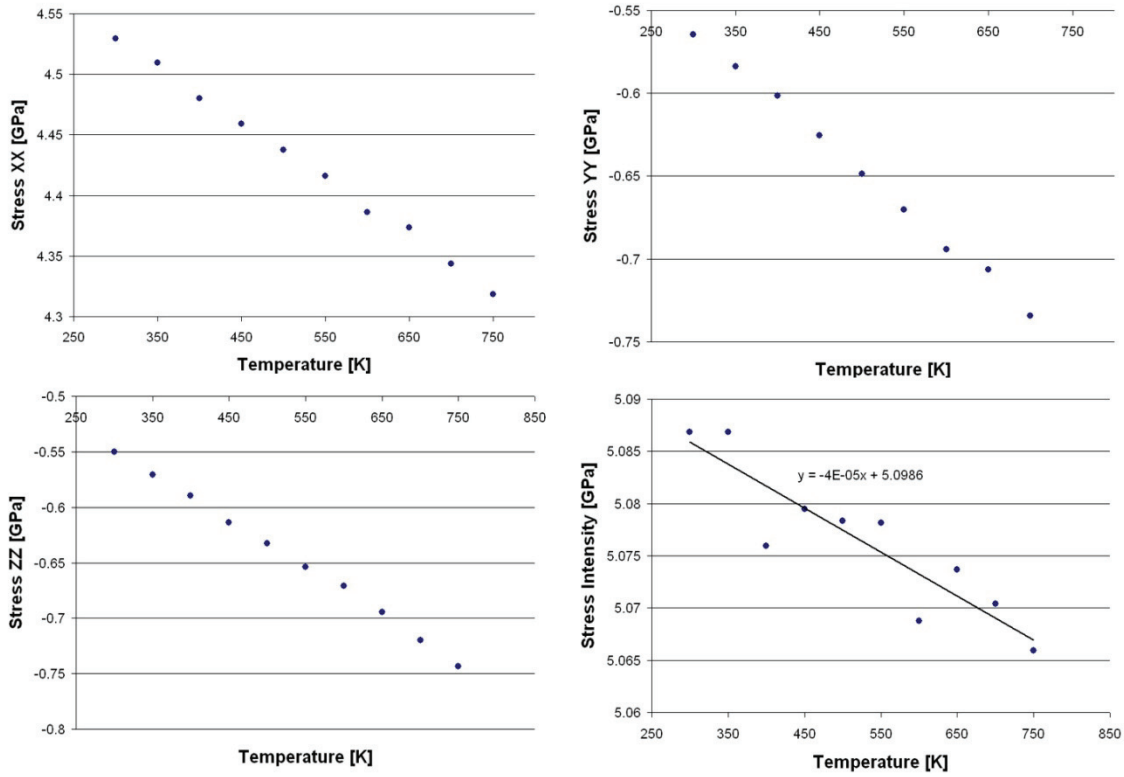

Fig. 6. *Stresses in Si-Ti coating.*

The stress σ_{xx} is inversely proportional to the substrate temperature starting from approximately 4.60 GPa for 200 K. Non-uniform titanium concentration produces tensile stresses σ_{xx}. High positive stress in a coating leads to expansion of a coating. Values of stresses: σ_{yy}, σ_{zz}, are negative and range from -0.7 to -0.5 GPa and getting lower with temperature increase. A relatively high compressive stress in coating is producing higher fracture toughness of the substrate. It is observed in higher temperatures, that bombarding ions loss less energy than in lower temperatures that leads to the reduction of stresses in the

7.2. Stress measurement results

The Raman spectrum is determined by using the software OMNIC developed by Thermo Electron Corporation. The spectrum picks, shown in figure 7, are described by using the concept of Voigt's function.

The variation of internal stress, evaluated from the equation (11), for $\Delta\omega = 0.140 cm^{-1}$ equals to -88 MPa.

Table. 1. *Silicon picks.*

Focus of the laser beam in Raman spectroscope	Peak Type	Center of pick X	Height	FWHH cm^{-1}	Area cm^{-1}
In silicon substrate	Voigt	520.129	260065.0313	1.9933	2480010.5000
Inside the intermediate layer	Voigt	520.269	755.4141	2.1161	5639.7910

where FWHH stands for the Full Width at Half Height.

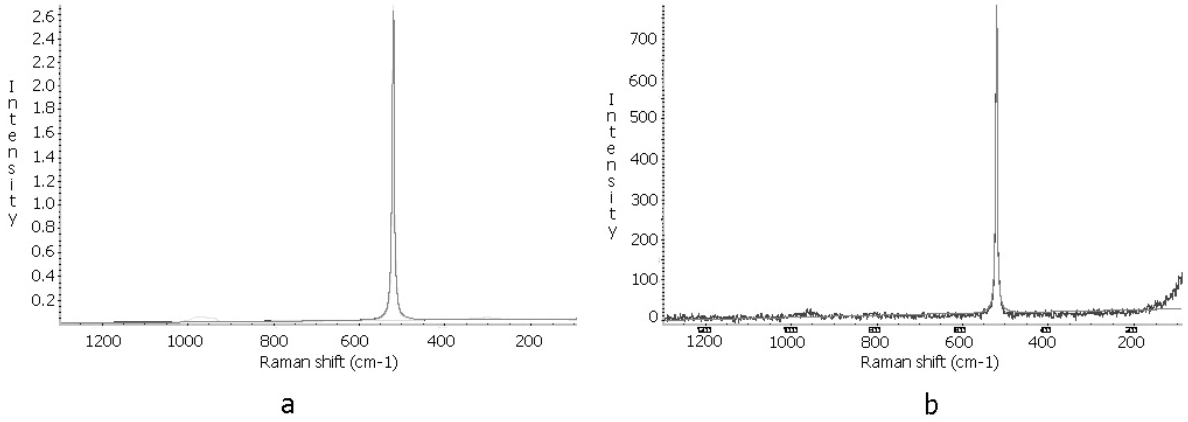

Fig. 7. *Raman spectrums for the silicon substrate (a) and inside the intermediate layer composed of Si and Ti atoms (b).*

8. CONCLUSIONS

A thin layer of titanium coating has been deposited on a silicon substrate and following that the significant difference of internal stress is observed between the substrate and the intermediate layer. This observation motivated the authors to investigate the possibility to determine residual stresses produced by IBSD methods. Two methods suitable for this purpose are identified: the first one utilizes successively three software packages: SRIM, TRIDYN and Cerius[2] , and the second one is based on the Raman spectrum shift measured firstly in a virgin substrate and secondly in the intermediate layer. The first method determines stress values through the thickness of a sample but the second method evaluates the difference stresses between the Ti/Si intermediate layer and Si substrate. The results can be compared only for one depth value. Such conclusion could be evaluated as very poor but it has a significant value because it gives the opportunity to verify data identified for numerical calculations and partial numerical results against physical measurements.

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ANALIZA NAPRĘŻENIA W POWŁOCE KRZEMOWO-TYTANOWEJ WYTWORZONEJ PRZEZ ROZPYLANIE JONOWE

Streszczenie

Artykuł ten poświęcony jest analizie naprężeń wewnętrznych wygenerowanych w powłoce krzemowej w czasie nakładania warstwy metodą rozpylania jonowego (NWMPJ), która została wykorzystana do wytworzenia powłoki tytanowej na powierzchni próbki wykonanej z krzemu. Warstwa pośrednia jest mieszaniną krzemu i tytanu i ma większą gęstość niż podłoże krzemowe. Naprężenie w warstwie przejściowej trudno jest zmierzyć ale można je obliczyć metodami numerycznymi. Łatwiejszym zadaniem jest zmierzenie różnicy naprężeń między warstwą pośrednią i krzemowym podłożem, co można wykonać przy użyciu mikro-spektroskopu Ramana.

Model numeryczny NWMPJ można przedstawić jako proces złożony z dwóch części: modelu sprężystych zderzeń atomów podłoża z jonami penetrującymi podłoże i modelu tworzenia struktury powłoki.

Przestawiony problem można numerycznie rozwiązać przy użyciu dwóch programów: SRIM i TRYDYN. Pierwsza część rozwiązania bazuje na obliczeniach sprężystych zderzeń dwucząsteczkowych (SZD), gdzie wykorzystano metodę Monte Carlo. Energia jonów penetrujących podłoże jest rozpraszana na skutek zderzeń z kolejnymi atomami podłoża. W następstwie tego można obserwować zmiany kąta rozpraszania dla cząstek. W każdej iteracji SZD oblicza się stratę energii cząstki atakującej. Rozkład gęstości warstwy pośredniej oblicza się w programie TRIDYN. Na podstawie tego rozkładu można określić strukturę powłoki używając programu Cerius^2, gdzie wykorzystano modele dynamiki molekularnej. Wyniki tych obliczeń pozwalają na określenie naprężeń wewnętrznych w powłoce.

Makroskopowe właściwości próbki Si-Ti określa się numerycznie przyjmując, że energia układu termodynamicznego w czasie obróbki warstwy wierzchniej zmienia się ale objętość układu jest stała. Taki układ termodynamiczny jest znany jako układ kanoniczny NVT (ciężar molowy (N), objętość (V) i temperatura (T)), gdzie energia procesów endotermicznych i egzotermicznych jest wymieniana z termostatem (termostat Nosé-Hoovera i dynamika Langevina). Proces powlekania jest kontrolowany przez następujące parametry: strumień wiązki rozpylonych atomów, temperatura podłoża i czas. Założono, że energia strumienia rozpylonych atomów jest równa 15 keV.

Submitted: November 4, 2008
Submitted in a revised form: December 11, 2008
Accepted: December 15, 2008