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Ion Beam Mixing in Metallic Superlattices

Mixing przy pomocy wiązki jonowej w supersieciach metalicznych

Смешивание ионным пучком в металлической сверхрешетке

Dedicated to Professor Stanisław Szpikowski
on occasion of his 60th birthday

INTRODUCTION.

Ion beam mixing has shown itself to be a practical and effective means of producing unique surface alloys [1]. This technique is capable of producing metastable crystalline and amorphous alloys as well as equilibrium alloys. The structures formed by ion mixing have been shown to be a function of several variables.

The earliest use of an ion beem to modify materials properties was initiated in the early sixties (the doping of semiconductors by ion implantation). Ten years later the study of ion implantation began to deal with metals. Ion implantation can modify various surface properties of metals and alloys, such as wear and corrosion resistances, superconductivity, etc. As a part of a program concerned with the use of energetic ion beams in the fabrication of metallic high energy laser mirrors D. Ingram and P. Pronko [2] have been studying the improvement in adhesion of a metal coating on a metal substrate when it is bombarded with an MeV ion beam following deposition.

In contrast to direct implantation ion mixing was introduced in early seventies. In this case, the ion beam is used to trigger atomic collisions for inducing intermixing between deposited material B and the matrix A, or both deposited A and B bilayer or multilayers and thus forming a uniform A-B alloy phase. Ion beam mixing of multilayers offers a novel technique to manufacture new alloy thin films with neither limitation of the alloy composition nor of the metal spacies required.

In the past five years more then thirty binary metal systems have so far been studied [1] by ion mixing of multilayers. Many studied alloys have not been produced or are even not obtainable by the traditional means. In the early eighties ion mixing of superlattices was introduced. In this paper we report ion beam mixing of Bi-Sb and Ag-Cu superlattices.

SAMPLE PREPARATION.

Bi-Sb and Ag-Cu superlattice samples were deposited on glass substrates in vacuum system equipped with a liquid nitrogen trap. The residual gass pressure was equal to $7 \cdot 10^{-7}$ Torr. The thickness of metal layers was controled by a programmable quartz thickness monitor with accuracy better than thickness of one atomic layer. In order to obtain the best crystal structure of Ag-Cu superlattice the temperature of the substrate was kept at 360 K. For the same reasons, for Bi-Sb superlattice samples the substrates were cooled to 173 K. The deposition rate of each element was typically 10 Å/sec.

IMPLANTATION PROCEDURE.

The superlattice samples were bombarded with 300 keV Ar^{++} and Kr^{++} ions at room temperature, up to a total doses of same 10^{15} ions/cm² at a pressure of 10^{6} Torr. In order to avoid an eventual beam heating phenomenon of the samples, a great care was taken to use extremaly low ion beam currents. Typically at the beginning we have 30 nA/cm² and it was increased up to 120 nA/cm² when reaching doses around 10^{15} ions/cm².

The ion energies were selected such that the ion mean projected range R_p at the noble gas is approximately the same as the total film thickness. For superlattice target A_yB_{100-y}, the projected range can be calculated by the following equation:

$$Rp(A_yB_{100-y}) = \frac{Rp(A)\cdot Rp(B)}{y\cdot Rp(B) + (100-y)\cdot Rp(A)}$$

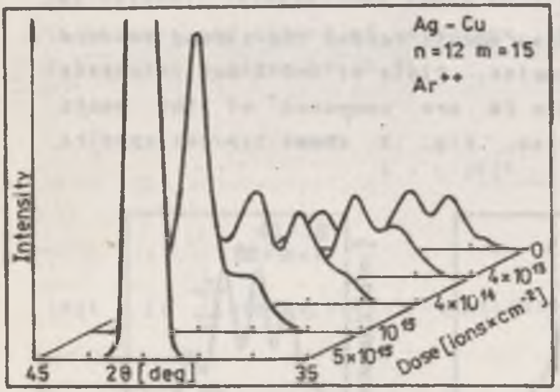

Fig. 1 X-ray diffraction spectra of Ag-Cu superlattice taken after each sequential implantation.

where y refers to the weight percentage of metal A in the superlattice.

During irradiation, the penetration of energetic ions through the diffrent interfaces A-B produces intermixed regions and the concenrations of the two elements A and B in the intermixed layer are close to that of a stable or metastable phase. As the irradiation proceeds the growth of the intermixed layers occurs [3] at the different interfaces and due to the geometry of the films, their thickness increases until the total mixing of all the couples is achieved (Fig. 1 and 2).

In order to study the kinetic behavior of the ion beam mixing process as a function of the ion dose, after each sequential implantation the crystal structure of superlattice samples was analysed from X-ray Bragg reflections.

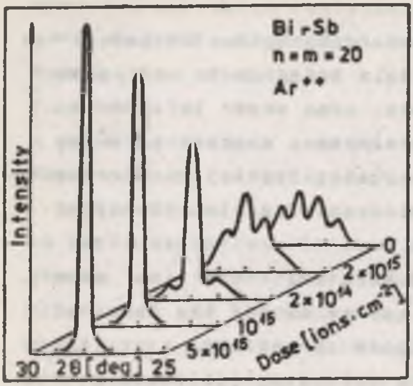

Fig. 2 X-ray diffraction spectra of Bi-Sb superlattice taken after each sequential implantation.

STRUCTURAL ANALYSIS.

The X-ray diffraction measurements reveal the strong texture in Bi-Sb and Ag-Cu layered samples. Plots of the X-ray intensity as a function of the angle 2θ are composed of the peaks characteristic of a superlattice. Fig. 3 shows typical spectra

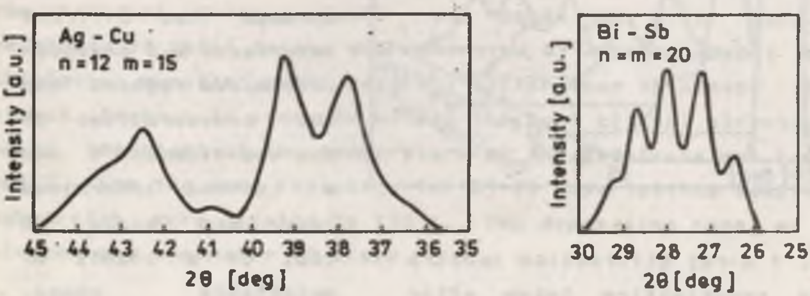

Fig. 3 Typical spectra of Ag-Cu and Bi-Sb superlattices.

of Bi-Sb and Ag-Cu layered samples with a total thickness about 1500 Å. n and m denote the numbers of atomic planes of metal A and B in one pair of layers.

To explain the X-ray diffraction properties of the superlattice samples we used a statistical model developed in our laboratory [4,5]. Our statistical model takes into account following factors:

1. composition of superlattices, designed thickness of individual layers n and m, superlattice period and random distribution of n and m, varying according to a gaussian distribution,
2. grain thickness and fluctuations of this thickness according to a gaussian distribution,
3. interface thickness which can extend over several interatomic distances.

Using computer program (based on Monte Carlo method) we can calculate positions, intensity and half-width of all Bragg peaks. Fitting observed diffraction patterns by statistical model we can get valuable informations about quality of superlattices, grain thickness and nature of interface. A general formula for X-ray intensity is given by [6,7]:

$$I = L \cdot |F|^2$$

$$|F|^2 = \Big|\Big[\sum_{j=1}^{n} \exp(-W_A \cdot s^2) \cdot g_A \cdot \exp(i4\pi s \cdot x_j) +$$

$$+ \sum_{j=1}^{m} \exp(-W_B \cdot s^2) \cdot g_B \cdot \exp(i4\pi s \cdot x_j) \Big]\Big|^2$$

where

$$L = \frac{1 + \cos^2(2\theta)}{\sin\theta \cdot \sin 2\theta} \quad , \quad S = \frac{\sin\theta}{\lambda}$$

$$g_A = f_A(\theta) \cdot \sigma_A \quad , \quad g_B = f_B(\theta) \cdot \sigma_B$$

and λ is the wavelenght of the X-ray, f_A and f_B are the scattering functions of atoms A and B, σ_A and σ_B are the density of atoms A and B in plane, W_A and W_B are the Debye-Waller coefficients, n is the number of A atomic planes in one layer, m is the number of B atomic planes in one layer, x_j' is the position of j-th atomic plane. As an example, typical structural factors of superlattices are shown in Table 1.

superlattice parameters	Bi - Sb	Ag - Cu
num. of monolayers I	20	12
num. of monolayers II	20	15
at. deviation	1,7	1,7
grain size	50	45
dev. of grain size	20	15
half interface	4	2

Table 1. Typical structural factors of Bi-Sb and Ag-Cu superlattices.

After each sequential implantation the crystallographic structure of Bi-Sb and Ag-Cu superlattice were investigated by θ-2θ X-ray diffraction.

RESULTS AND DISCUSSION.

By irradiating superlattice samples with various doses (in our case from 10^{5} to $5\cdot10^{6}$ ions/cm^{2}) and identyfying the structure by X-ray diffraction it was possible to examine the intermediate states of transformation. Fig. 1 and 2 shows as an example X-ray diffraction spectra of samples taken after each sequential implantation. From X-ray spectra is clear that we formed Bi-Sb and Ag-Cu alloys from superlattice samples by ion implantation. To our knowladge it is the first such type of an experiment where solid solution have been formed from metallic superlattices of Bi-Sb and Ag-Cu.

Ion beam induced atomic mixing of the interference of thin films has been one of the attractive topics in ion beam modification of material during the past five years. However, from the atomic point of view the basic physical mechanisms of ion beam mixing in layered solids are not very well understood. In general often more than one mechanism appears to be contributing to mixing phenomena. At last two types of elementary atomic processes are involved during ion beam mixing and three general classes of models have been proposed:

1. Equilibrium models which describe transport resulting from thermal migration of atoms in a high concetration of defects.
2. Ballistic model in which the transport is the product of the radiation damage itself.
3. Phenomenological model where ion beam mixing is a combined effect of both ballistic mixing and diffusional mixing [8].

From experimental point of view it is important to know haw the number of intermixed atoms Q depends on the fluence Φ. Unfortunately all three models for ion beam mixing are not good enough to explain the observed ion mixing phenomena. In the backscattering studies of ion beam mixing it was found that:

$$Q = A \cdot \phi^{\alpha}$$

As the irradiation proceeds the growth of the intermixed layers occurs, until total mixing is achieved. It means that the intensity of alloy X-ray peak must be a function of fluence ϕ:

$$I = f(\phi).$$

Such variations have indeed been observed and is shown on Fig. 4 a,b,c. During the implantation a pronounced increase of the grain size could observed as it is shown on Fig. 5 a,b.

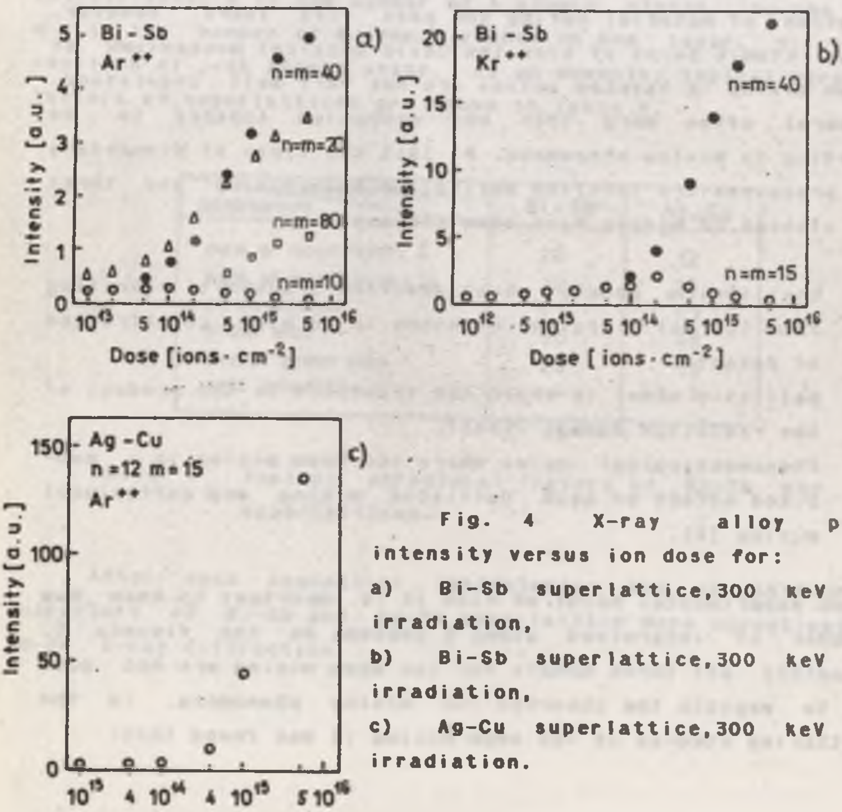

Fig. 4 X-ray alloy peaks intensity versus ion dose for:

a) Bi-Sb superlattice, 300 keV Ar⁺⁺ irradiation,

b) Bi-Sb superlattice, 300 keV Kr⁺⁺ irradiation,

c) Ag-Cu superlattice, 300 keV Ar⁺⁺ irradiation.

The main point of this investigations are:

1. The kinetic behaviour of the ion mixing in superlattice samples can be studied by analysis of X-ray diffraction spectra.
2. For the first time Bi-Sb and Ag-Cu alloys have been formed from superlattice by ion beam technique.
3. In all cases a strong texture have been observed.
4. We found a pronounced increase of the grain size when ion dose increases.

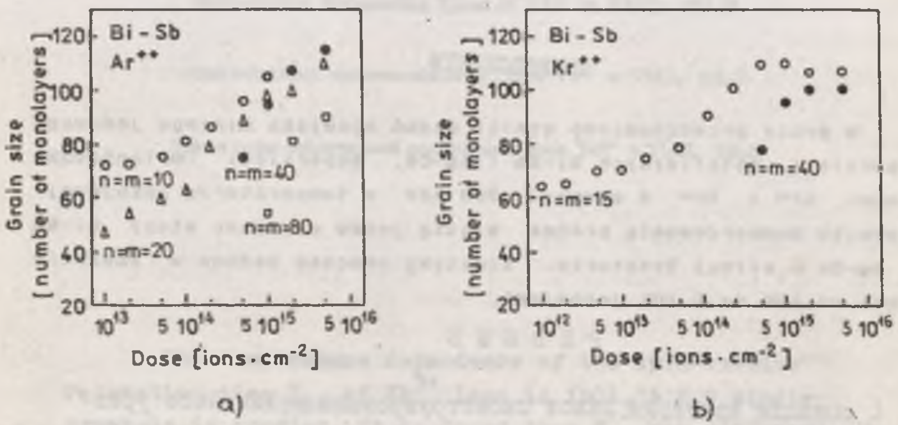

Fig. 5 Grain size of Bi-Sb superlattice versus ion dose for: a) 300 keV Ar^{++} irradiation, b) 300 keV Kr^{++} irradiation.

Presented here raport is a part of a program concerned with the investigations of metallic superlattices (under grant CPBP 01.08.C3.1 sponsored by Ministry of Science and Education). Cleary more investigations is needed and some new results will be published soon.

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STRESZCZENIE

W pracy przedstawiono wyniki badań zjawiska mixingu jonowego supersieci metalicznych Bi-Sb i Ag-Cu. Supersieci implantowano jonami Ar^{++} i Kr^{++} o energii 300 keV w temperaturze pokojowej. W wyniku bombardowania próbek wiązką jonów uzyskano stopy Bi-Sb i Ag-Cu o silnej teksturze. Kinetykę procesu badano w zakresie dawek od 10^{15} do $5\cdot10^{15}$ jonów/cm^2.

РЕЗЮМЕ

С помощью критерия Лакса сконструировано нелинейное уравнение Кортвега-де Бриса пятой степени. Для получения односолитонного решения этого уравнения применен обратный метод рассеяния.