

## Effects of Platinum on the Inter-diffusion of Titanium-Gold Based Alloys

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### □ ABSTRACT □

Rutherford Backscattering used is a method to study the surface composition of the compound ( between  $X = 0$   $\mu \rightarrow$  many microns ) in depth. The energy analysis of the scattered particles due to collision with the target, will allow us to differentiate between the mass M of that target and its density inside it.

Interdiffusion in the systems is measured using Rutherford backscattering. Extensive grain size measurements are used to interpret the data in terms of grain-boundary-assisted bulk diffusion. At room temperature, rapid grain-boundary diffusion of Au into the fine-grained Pt layer of the Ti-Pt-Au films occurs, characterized by a diffusion coefficient. The bulk diffusion of Au into the grains of the Pt film layer is examined. It is found that interdiffusion in Ti-Pt couple is much slower than in Ti-Au.

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## تأثير البلاتين على عملية الانتشار المتبادل في الخلائط ذات الأساس " تيتان - ذهب "

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### □ الملخص □

إن طريقة RBS هي طريقة تحليلية لسبر المناطق القريبة من السطح (من  $x=0$  إلى بضعة ميكرونات عمقاً). إن التحليل الطاقى للجزيئات المرتدة عن التصادم مع ذرات الهدف (العينة) تسمح بتمييز الكتل  $M$  لذرات الهدف ، ووضعها داخل الجزيئة وتركيزها. تمت دراسة الانتشار المتبادل في الأفلام الرقيقة من النوع  $Ti/Pt/Au$  باستخدام طريقة الاستطارة الخلفية لرذرفورد. لقد استخدم قياس حجم الحبيبات، وذلك بغية شرح المعطيات على شكل انتشار الحبيبات في منطقة الحدود في الجملة.

ففي درجات الحرارة العادية، تم وصف الانتشار السريع لحبيبات الذهب المجاورة لدقيق حبيبات البلاتين في أفلام  $Ti/Pt/Au$  ، بمعامل الانتشار . تمت في الجملة عملية فحص انتشار الذهب في حبيبات البلاتين. لقد تبين أن عملية الانتشار المتبادل في الأفلام الزوجية لـ  $Ti/Pt$  هي أكثر بطأً منها في الأفلام الزوجية لـ  $Ti/Au$ .

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## 1. INTRODUCTION

The components of a backscattering system are shown in Figure 1. The source generates a beam of collimated and monoenergetic particles of energy  $E_0$ . A typical case the experiment conditions are a current of 10 to 100 nA , and an energy beam of 2.0-MeV  $\text{He}^+$  ions in a  $1\text{-mm}^2$  area. These particles impinge on the sample (or target) which is the object to be analyzed. Almost all of the incident particles come to rest within the sample.

Avery few particles (much less than  $\frac{1}{10^4}$ ) are scattered back out of the sample. Of these, a small fraction is incident on the area defined by the aperture of an analyzing system. The output of that system is an analog signal. This signal is processed by a multichannel analyzer, which subdivided its magnitude into a series of equal increments. Each increment is numbered and referred to as a channel. Modern multichannel analyzers contain thousands of channels. An event whose magnitude falls within a particular channel is registered there as a count. At the termination of the experiment, each channel has registered a certain number of counts. The output of the multichannel analyzer is thus a series of counts contained in the various channels.

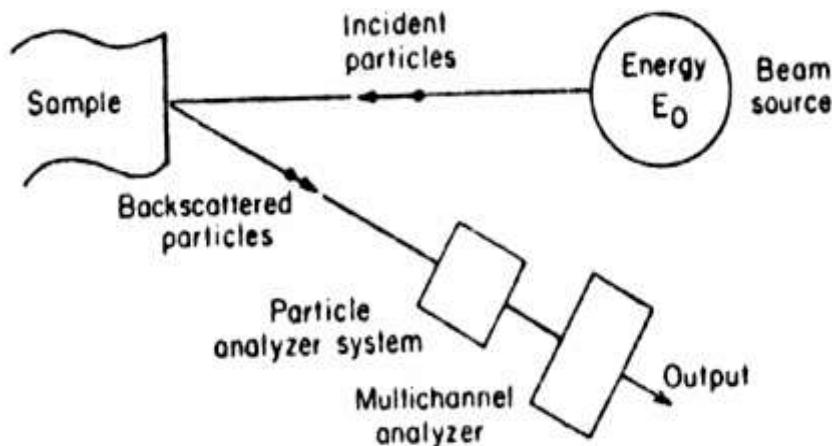


Fig.1: Conceptual layout of backscattering spectrometry system.

Many of the properties of materials in film form differ markedly from those of the same materials in the bulk. The widespread use of thin films in electronic and optical devices has stimulated interest in a detailed understanding of diffusional processes in film, since these processes affect the long-term stability of multicomponent film structures. A wide variety of techniques have been used in the past to derive information on film interdiffusion rates. For the most part, however, measurements have been of some property change indirectly related to the diffusivity, such as electrical conductivity and optical reflectivity, and there is a paucity of quantitative film diffusion data, even for metallurgically simple systems.

Rutherford backscattering offers a powerful technique for determining directly [1-4], and with good resolution, compositional profiles in complex multicomponent film structures undergoing diffusion anneals. In this work, we have applied backscattering to

the study of multilayer of Au- based metallization schemes of a type frequently used to interconnect components on integrated circuits. Gold has many attractions for use as a thin-film conductor on integrated circuits because of its excellent conductivity, lack of oxidation, and resistance to electro migration failures. However, the fact that Au is so uncreative also means that it does not adhere well to dielectrics

[5-7]. Interdiffusion in the ternary metallization Ti/Pt/ Au , Platinum is attractive as a diffusion barrier layer because its conductivity is higher than that of either Pt and because its high melting point suggests that multilayer systems containing it may have superior thermal stability[8]. To overcome this a metallic layer such as Ti is introduced. Unfortunately the Ti/Au couple is susceptible to corrosion and a passivating or barrier metal such as Pt. Clearly, interdiffusion among three layers can result in:

- 1- loss of conductivity.
- 2- loss of corrosion passivation.
- 3- loss of adhesion between the titanium layer and the substrate.

Further potential hazards are instabilities resulting from the formation of layers of intermediate phases. A primary objective has been to understand and characterize thin-film interdiffusion in the simple Pt/Au system. The Rutherford backscattering technique provides interdiffusion profiles with a depth resolution of some  $150 \text{ \AA}$  along the direction of the incident beam. However, the lateral beam spread is  $\sim 1 \text{ mm}$  in width. In the Ti/Pt/Au system Ti is next to the substrate and Au is the outer most layer. The RBS method used is an analysis one to study the composition of regions of the surface (between  $x=0 \rightarrow$  many microns in depth. The sample analyzed (Fig.1) is bombarded with beam monoenergetic particles ( $\text{H}^+$  ,  $\text{He}^+$  ...). The energy analysis of the scattered particles due collision with the target will allow us to differential between the mass  $M$  of that target, and its density inside it as well as their position in depth and their concentration. The amount of particles beam energy is of the order (MeV) and of scattered angle varies between ( $150^\circ - 180^\circ$ ). In Rutherford backscattering spectrometry, monoenergetic particles in the incident beam collide with target atoms and are scattered backwards into the detector—analysis system which measures the energies of the particles. In the collision, energy is transferred from the moving particle to the stationary target atom; the reduction in energy of the scattered particle depends on the masses of incident and target atoms and provides the signature of the target atoms. The energy transfers or kinematics in elastic collisions between two isolated particles can be solved fully by applying the principles of conservation of energy and momentum. For an incident energetic particle of mass  $M_1$  , the values of the velocity and energy are  $V$  and  $E_0$  ( $E_0 = 1/2 M_1 V^2$ ) while the target atom of mass  $M_2$  is at rest. After the collision, the values of the velocities  $V_1$  and  $V_2$  and energies  $E_1$  and  $E_2$  of the projectile and target atoms are determined by the scattering angle  $\theta$  and recoil angle  $\phi$ .

Conservation of energy and conservation of momentum parallel and perpendicular to the direction of incidence are expressed by the equations

$$\frac{1}{2} M_1 V^2 = \frac{1}{2} M_1 V_1^2 + \frac{1}{2} M_2 V_2^2 \quad (1)$$

$$M_1 V = M_1 V_1 \cos \theta + M_2 V_2 \cos \phi \quad (2)$$

$$0 = M_1 V_1 \sin \theta - M_2 V_2 \sin \phi \quad (3)$$

Eliminating  $\phi$  first and then  $V_2$ , one finds the ratio of particle velocities

$$\frac{V_1}{V} = \left[ \pm (M_2^2 - M_1^2 \sin^2 \theta)^{\frac{1}{2}} + M_1 \cos \theta \right] / (M_1 + M_2) \quad (4)$$

The ratio of the projectile energies for  $M_1 < M_2$ , where the plus sign holds, is

$$\frac{E_1}{E_0} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{\frac{1}{2}} + M_1 \cos \theta}{M_1 + M_2} \right]^2 \quad (5)$$

The energy ratio, called the kinematic factor  $K = E_1/E_0$ , shows that the energy after scattering is determined only by the masses of the particle and target atom and the scattering angle. A subscript is usually added to  $K$ , i.e.,  $K_{M_2}$ , to indicate the target atom mass.

For direct backscattering through  $180^\circ$ , the energy ratio has its lowest value given

by 
$$\frac{E_1}{E_0} = \left( \frac{M_2 - M_1}{M_2 + M_1} \right)^2 \quad (6)$$

and at  $90^\circ$  is given by

$$\frac{E_1}{E_0} = \frac{M_2 - M_1}{M_2 + M_1} \quad (7)$$

In collisions where  $M_1 = M_2$ , the incident particle is at rest after the collision with all the energy transferred to the target atom, a feature well known in billiards. For  $\theta = 180^\circ$ , the energy  $E_2$  transferred to the target atom has its maximum value given by

$$\frac{E_2}{E_0} = \frac{4M_1M_2}{(M_2 + M_1)^2} \quad (8)$$

with the general relation given by 
$$\frac{E_2}{E_0} = \frac{4M_1M_2}{(M_2 + M_1)^2} \cos^2 \phi \quad (9)$$

In practice, when a target contains two types of atoms that differ in their masses by a small amount  $\Delta M_2$ , the experimental geometry is adjusted to produce as large a change  $\Delta E_1$  as possible in the measured energy  $E_1$  of the projectile after the collision. A change of  $\Delta M_2$  (for fixed  $M_1 < M_2$ ) gives the largest change of  $K$  when  $\theta = 180^\circ$ . Thus  $\theta = 180^\circ$  is the preferred location for the detector ( $\theta \cong 170^\circ$  in practice because of detector size) – an experimental arrangement that has given the method its name of backscattering spectrometry.

The identity of target atoms is established by the energy of the scattered particle after an elastic collision. The number  $N_S$  of target atoms per unit area is determined by the probability of a collision between the incident particles and target atoms as measured by the total number  $Q_D$  of detected particles for a given number  $Q$  of particles incident on the target in the geometry shown in Figure 2. The connection between the number of target atoms  $N_S$  and detected particles is given by the scattering cross section. For a thin target of thickness  $t$  with  $N$  atoms/cm<sup>3</sup>,  $N_S = Nt$ .

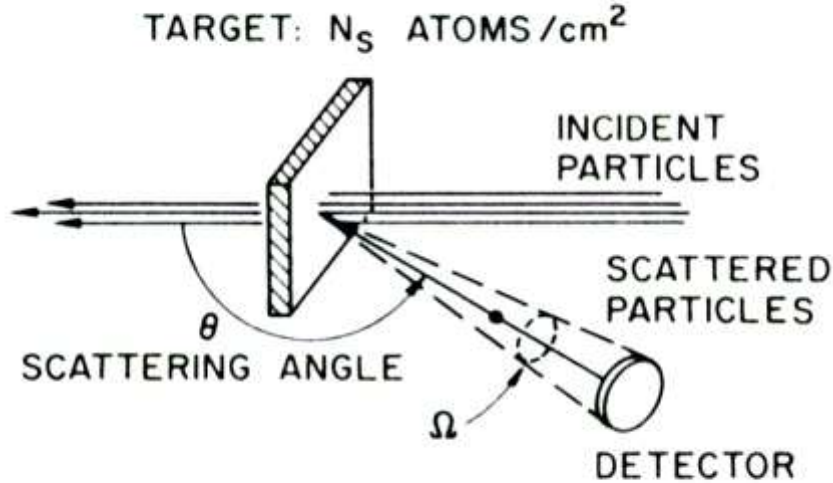
The differential scattering cross section,  $d\sigma/d\Omega$ , of a target atom for scattering an incident particle through an angle  $\theta$  into a differential solid angle  $d\Omega$  centered about  $\theta$  is given by

$$\frac{d\sigma(\theta)}{d\Omega} \cdot d\Omega \cdot N_S = \frac{\text{Number of particles scattered into } d\Omega}{\text{Total number of incident particles}} \quad (10)$$

In backscattering spectrometry, the detector solid angle  $\Omega$  is small ( $10^{-2}$  steradian or less) so that one defines an average differential scattering cross section  $\sigma(\theta)$ ,

$$\sigma(\theta) = \frac{1}{\Omega} \int_{\Omega} \frac{d\sigma}{d\Omega} \cdot d\Omega \quad (11)$$

Where  $\sigma(\theta)$  is usually called the scattering cross section. For a small detector of area  $A$  at a distance  $L$  from the target, the solid angle is given by  $A/L^2$  in steradians. For the geometry of Figure 2, the number  $N_S$  of target atoms/cm<sup>2</sup> is related to the yield  $Y$  or the



**Fig. 2 Simplified layout of a scattering experiment to demonstrate the concept of the differential scattering cross section Only primary particles that are scattered within the angle  $d\Omega$  spanned by the detector are counted.**

Number  $Q_D$  of detected particles (in an ideal, 100% efficient detector that subtends a solid angle  $\Omega$ ) by  $Y = Q_D = \sigma(\theta) \cdot \Omega \cdot Q \cdot N_S \quad (12)$

Where  $Q$  is the total number of incident particles in the beam. The value of  $Q$  is determined by the time integration of the current of charged particles incident on the target. From Eq. (12) one can also note that the name "cross section" is appropriate in that  $\sigma(\theta)$  has the dimensions of an area.

The scattering cross section can be calculated from the force that acts during the collision between the projectile and target atom. For most cases in backscattering spectrometry, the distance of closest approach during the collision is well within the electron orbit so that the force can be described as an unscreened Coulomb repulsion of two positively charged nuclei with charge given by the atomic numbers  $Z_1$  and  $Z_2$  of the projectile and target atoms. We consider here the thermal stability of the metallization systems Ti-Pt-Au. Preliminary results [8] on interdiffusion in the Ti-Pt-Au system showed several interesting effects which are explored at greater length in the current work. In particular, we verify the presence of Au in the Pt layer of unannealed Ti-Pt-Au films and show that room-temperature diffusion, presumably along grain boundaries, is responsible for its occurrence there. Platinum is attractive as a diffusion barrier layer because its

conductivity is higher than that of either and because its high melting point suggests that multilayer systems containing it may have superior thermal stability. The diffusion profiles for this study were measured by Rutherford backscattering of 1.8-MeV  ${}^4\text{He}^+$  ions. This technique is particularly well suited to thin-film analysis as it yields a depth resolution of 100 - 150 Å and is useful for thickness up to several thousand Å. Since the transverse resolution of Rutherford backscattering is ~1 mm the diffusion profiles have been analyzed in conjunction with transmission electron microscopy measurements of film grain structure.

## 2. EXPERIMENTAL

### 2.1 Sample preparation :

We prepared thin layer ( one layer over the another ) form Ti, Pt and Au over a Si[111] disc, covered by another of carbon thin layer. This is to avoid spectrum lines-peaks ( RBS ). The films used in this study were deposited in an electron-beam evaporator, annealed in vacuum, and examined by Rutherford backscattering as described in [9]. Typical deposition rates were 8 Å/sec for Pt , 12 Å/sec for Au and 25 Å/sec for Ti. Double-layer Pt-Au and Au-Pt films could not be used here because of poor adhesion and stress effects; however, Ti-Pt-Au and Ti-Au-Pt films were prepared. To characterize the structure of the films, grain size measurements and electron diffraction patterns were obtained using a 100-keV transmission electron microscope. For these measurements 700 - Å metal films were evaporated separately onto oxidized Si wafers, annealed in air, and then stripped from the substrates for microscopy. A number of composite Ti-Pt-Au films were also stripped from the substrates after annealing and then selectively etched to allow the individual films to be viewed separately in the electron microscope.

### 2.2 Investigation of reaction products:

In order to investigate the depth distribution , RBS was used and measured using 1.8-2.0 MeV  ${}^4\text{He}^+$  ions at a backscattering angle of typically  $170^\circ$ . The energy resolution was 3 keV/ channel. Au depth profiles were obtained from the RBS spectra using the RUMP simulation code[10 ].

## 3. RESULTS AND DISCUSSION

Backscattering spectra from a Ti/Pt/Au composite are shown in Fig. 3. The Pt/Au layer is seen to undergo considerable interdiffusion, whereas there is no discernible interdiffusion of Ti into the Pt layer.

Over the lower-temperature range ( $<400^\circ\text{C}$ ) in which most of the anneals in the present

Experiments were performed interdiffusion between the Ti and in Pt films the two- and three - layer structures occurred at a very low level or was unobservable. Thus, the Ti film layer was assumed to provide adhesion to the substrate without materially effecting the interdiffusion between the Pt and the Au in the Ti-Pt-Au films. Equivalent air anneals for the Ti-Pt show correspondingly small levels of interdiffusion, in contrast to the differences in vacuum and air annealed Ti-Au.

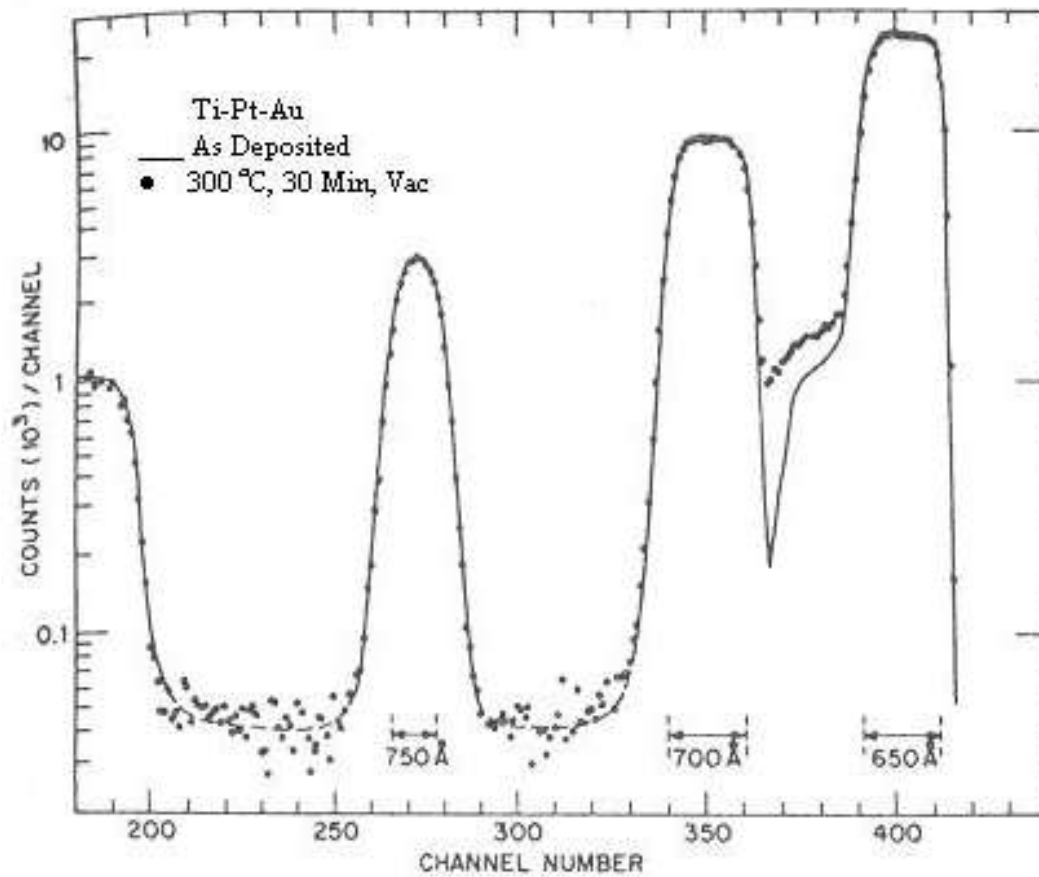


Fig.3. Backscattering spectra of Ti-Pt-Au before (line) and after (open circles) annealing at 300 °C for 30 min in vacuum.

The shoulder on the low energy side of the preanneal Au peak is thought to result from room-temperature grain-boundary diffusion of Au into Pt. The postanneal spectrum shows an increase in the level of Au in Pt with no appreciable amount of Pt diffusing into the Au layer. The backscattering results for annealed Ti-Pt show little or no discernible interdiffusion between Ti and Pt. The backscattering results for Ti-Pt-Au indicate no discernible Ti-Pt interdiffusion at temperatures  $\leq 400$  °C but there is considerable Au diffusion into the Pt layer. Moreover diffusion, for temperatures  $\leq 400$  °C, proceeds in only one direction with Au diffusing into the Pt with virtually no Pt diffusing into the Au film layer.



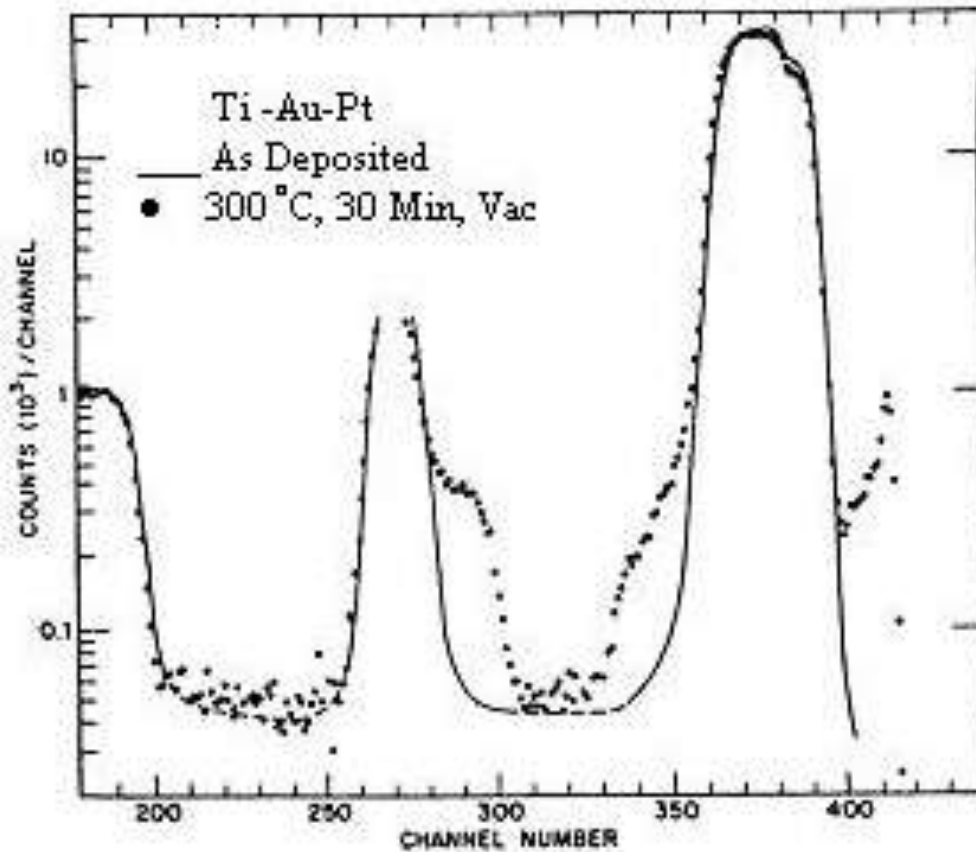


Fig. 4. Backscattering spectra of Ti-Au-Pt before (line) and after (open circles) annealing at 300 °C for 30 min in vacuum.

Figure 4 shows the spectra from such a reverse evaporation. The Au and Pt diffusion profiles should be the mirror images of those shown in Fig. 3. Comparison of Figs.3 and 4 shows that the interdiffusion depends strongly upon the order of the depositions in this system. In the postanneal spectrum of Fig. 4, the Au has diffused through the Pt and accumulated at the free surface of the film as shown by the sharp peak on the right. The Au surface peak shown in Fig. 4 corresponds to approximately one monolayer of Au on the free surface of the Ti-Au-Pt film. The Au presumably reaches the surface by grain-boundary diffusion followed by rapid surface diffusion. This surface diffusion may be driven by a surface segregation mechanism. Ti has diffused strongly into the Au layer during annealing and the tall on the low-energy side of the composite Au-Pt peak corresponds to Pt in the Au layer. The appearance of Au in the Pt component of unannealed Ti-Pt-Au films (Fig. 5) raised the question whether this Au diffusion took place during or subsequent to the film deposition as the films had aged for several weeks at room temperature before the spectra were taken. To elucidate the process by which the Au diffusion took place, a fresh set of Ti-Pt-Au films was prepared. During deposition, it was observed that the substrate temperature did not rise more than 20 °C above room temperature.

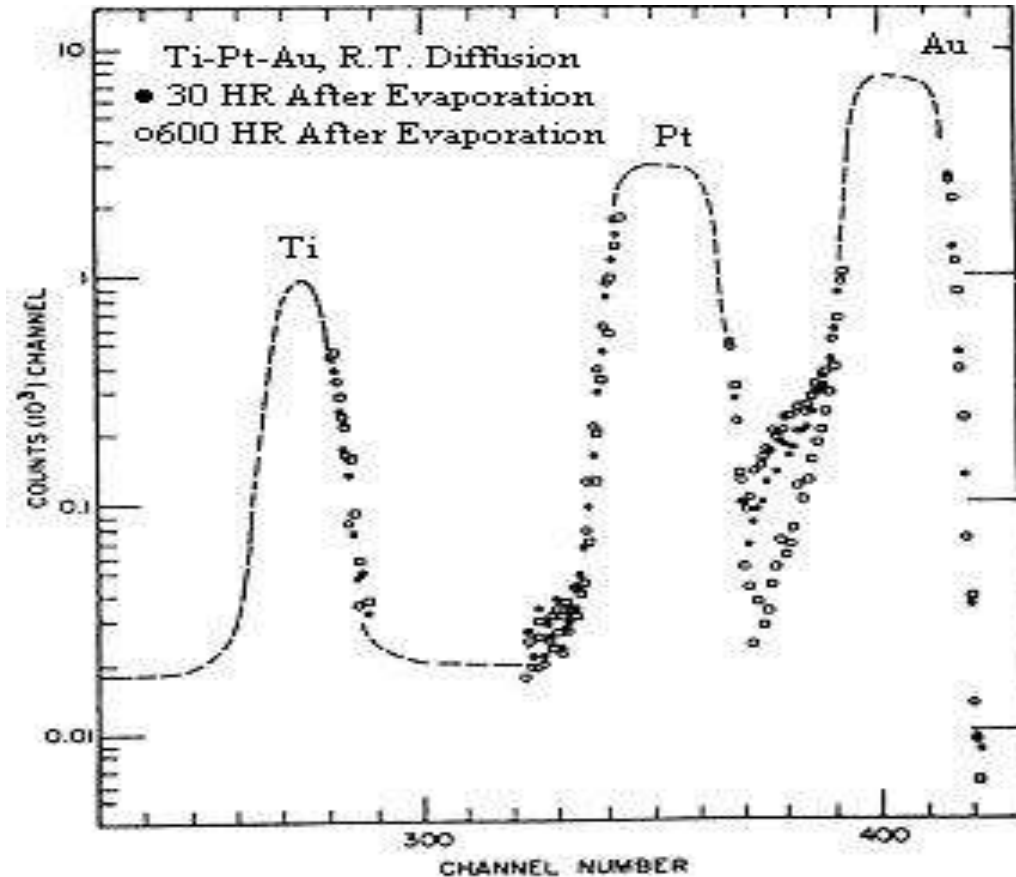


Fig. 5. Backscattering spectra of Ti-Pt-Au after aging at room temperature for times up to 600 h

#### 4. SUMMARY AND CONCLUSIONS

We have investigated interdiffusion in Ti/Pt/Au and the various couples that comprise this ternary thin-film system. The Au/Pt and Pt/Au interdiffusion profiles are not very sensitive to the annealing ambient (vacuum or air); the slight increase in the amount of interdiffused material for the air anneals is believed to be due to inhibition of grain growth during annealing. Strong ambient effects, however, are observed for the Ti/Au and Ti/Pt couples[11]. Air annealing, as compared to vacuum, enhances diffusion in Ti/Au and inhibits diffusion in Ti/Pt. The Ti-Pt couple exhibit very low levels of interdiffusion for temperatures  $\leq 400$  °C. Interdiffusion in the Ti-Pt-Au system is characterized by Au diffusion into Pt but no measurable Pt diffusion into Au for temperatures  $\leq 400$  °C. The Au is observed to diffuse along Pt grain boundaries at room temperature. On annealing Au is observed diffusing from the grain boundaries into the Pt grains. Analysis of this diffusion gives lattice diffusion constants that are anomalously low for fcc lattices possibly as a result of surface segregation, solid solubility, and/or stress effects[12].

Interdiffusion in Ti-Au-Pt is very different than Ti-Pt-Au. There is substantial interdiffusion of the Ti-Au and Au diffuses out to the Pt free surface. This surface segregation is compared with other data and theories of surface segregation in binary alloys.

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