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Studying the Interdiffusion of Thin-Films. Ti/Mg, Ti/Pt, Ti/Au, and Ti/Pd

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□ ABSTRACT □

Rutherford Backscattering spectroscopy (RBS) is used to study the interdiffusion in Ti/P, Ti/Au, Ti/Pt, and Ti/Mg thin film systems induced by thermal annealing. Bilayer films of Titanium, Palladium, Gold, Platinuium and Magnesium were prepared in vacuum by evaporating sequential deposition Pd and Au, Pt, Mg on Ti in Air, are compared with vacuum, annealing enhances interdiffusion in the Ti/Au. The compound TiAu4 could be identified by TEM. However, neither backscattering nor electron diffraction indicate compound formation in Ti/Pd system. The RBS spectra were analysed using the RUMP simulation code. The activation energy for this reaction was 1.14 ev.

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دراسة الانتشار المتبادل في الأفلام الرقيقة Ti/Pd,Ti/Au,Ti/Pt,Ti/Mg

الدكتور سمير غالية*

(قبل للنشر في 2002/12/15)

□ الملخّص □

استخدمت طريقة الاستطارة الخلفية لرذرفورد RBS لدراسة الانتشار المتبادل في الأفلام الرقيقة التالية: Ti/Pd;Ti/Au;Ti/Pt;Ti/Mg. التي حصلنا عليها بطريقة التحمية الحرارية.

حضرت أفلام من طبقتين وهما التيتانيوم وكلٍ من البلاد يوم،الذهب، بلاتينيوم والمغنيزيوم من جهة أخرى، وذلك بتبخيرها في الخلاء بتوضع التيتان على العناصر المذكورة أعلاه على التوالي: بإجراء عملية مقارنة بين التبخير في الهواء والتبخير في الخلاء، أمكن اكتشاف تنشيط الانتشار المتبادل في أفلام Ti/Au. يمكننا التأكد من هوية المركب المتكون من Ti/Au_4 بواسطة حيود الالكترونات TEM. دلت نتائج طريقة الاستطارة الخلفية وطريقة حيود الإلكترونات على عدم تشكل أي مركب في الجملة Ti/P. حللت أطيافRBS البيانية باستخدام برنامج "RUMP" وقد وجد أن طاقة تنشيط التفاعل هي 1.14 ev.

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1. Introduction

Rutherford backscattering is quite a simple experimental method [1,5]. In this case, monoenergetic and collimated alpha particles(^4He ions) incident beam collide with target atoms. the instrumentation is simple (Fig.1). knowing the stopping power, (dE/dx)(E)(with units MeV cm^2mg^{-1}), the ratio of the energy of the scattered particle, E_1/E_0, the thickness of material δ x of a spectral energy increment δE is given by[6]:

$$\delta\chi \cong \delta E\left[\frac{dE}{d\chi}(E_0)\frac{E_1}{E_0}+\frac{1}{|\cos\theta_L|}\frac{dE}{d\chi}(E_1)\right]^{-1} \quad (1)$$

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

The energy ratio, called the kinematic factor $K=\frac{E_1}{E_0}$

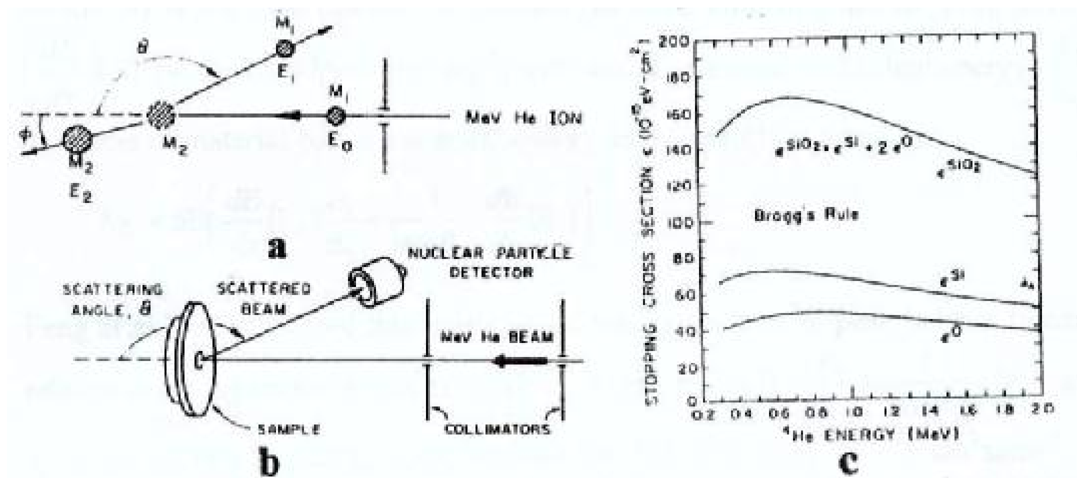

Figure 1. (a) Schematic representation of on elastic collision between a projectile of mass M_1,velocity v, and a target of mass M_2 and energy E_0=0, which is initially at rest. After the collision, the projectile and the target mass have velocities and energies v_1, E_1, and v_2, E_2, respectively. The angles θ and Φ are positive and shown. All quantities refer to a laboratory frame of reference. (b) simplified layout of a scattering experiment to demonstrate the concept of the differential scattering cross section. Only primary particles that are scattered within the solid angle spanned by the detector are counted. (c) Stopping cross section for ^4He ions in Si, O, and SiO_2. The oxide stopping cross section was

determined on a molecular basis ε^{SiO2}, on the assumption that Bragg's rule of linear additivity hold with 2.3×10^{22} SiO_2 molecules/cm^3

Scattering Cross Section σ

In the following expression [7]

$$\frac{d\sigma}{d\Omega} = 1.296\left(\frac{Z_1 Z_2}{E_0}\right)^2 \left[\mathrm{COS}^4\left(\frac{\theta_L}{2}\right) - 2\left(\frac{M_1}{M_2}\right)^2 + \ldots\right] \times 10^{-27}\,\mathrm{cm}^2 \qquad (3)$$

E_0 is the incident laboratory energy, Z_1, M_1 and Z_2, M_2 are the projectile and target atomic number and masses, respectively, and θ_L is the laboratory scattering angel. The next term in the expansion is of the order $\left(\frac{M_1}{M_2}\right)^2$ and may usually be neglected [3]. The backscattered yield from a target of thickness δx and density N_2 (atoms cm^{-3}) into a detector of solid angel $\Delta\Omega$ is given by[8]: $Y = N_1 (N_2 \delta x) \frac{d\sigma}{d\Omega} \Delta\Omega$, where N_1 is the total number of incident particles. Knowing the stopping power [9], $\left(\frac{dE}{dx}\right)(E)$ (with units MeV cm^2 mg^{-1}) and ratio of scattered to incident energy, $\frac{E_1}{E_0}$, the thickness of material δx in a spectral energy increment δE is given by:

$$\delta x \approx \delta E \left(\frac{dE}{dx}(E_0)\frac{E_1}{E_0} + \frac{1}{|\cos\theta_L|}\frac{dE}{dx}(E_1)\right)^{-1}$$

Fin get al. [10] have used this technique of taking the ratio of peak heights to compare relative stopping cross-section factors[ε],where $[\varepsilon] = \varepsilon(E_0)\frac{E_1}{E_0} + \frac{1}{|\cos\theta_L|}\varepsilon(E_1)$ and the ε ' s are the atomic stopping cross sections[11-12] with units of eV cm^2 $atom^{-1}$. From braggs rule[13] we can construct the relative atomic stopping cross sections of compounds. Consider an alloy A-B with atomic densities N_A and N_B (atomic densities N_A and N_B (atomic/cm^3). Then

$$\varepsilon_{A-B} = \frac{N_A}{N_A + N_B}\varepsilon_A + \frac{N_B}{N_A + N_B}\varepsilon_B \qquad (4)$$

It can be shown [14] that the ratio of yields from A before annealing to that after formation of the compound A-B is given by[7]

$$\frac{Y_A^A}{Y_{A-B}^A} = \frac{N_A + N_B}{N_A} \frac{\left[e_{A-B}^A\right]}{\left[e_A^A\right]} = 1 + \frac{N_B}{N_A} \frac{\left[e_B^A\right]}{\left[e_A^A\right]} \qquad (5)$$

The stopping cross section $e^{A_mB_n}$ of a solid of composition A_mB_m is given by $e^{A_mB_n} = me^A + ne^B$, where ε^A and ε^B are the stopping cross section of the atomic constituents A and B. To take a specific example of SiO_2 on a molecular basis, $e^{SiO_2} = e^{Si} + 2e^o$, where ε^{SiO2} is now the stopping power / molecule so that $\frac{dE}{dC} = Ne^{SiO_2}$,where N is the number of molecules /volume. Fig. 1.c shows the stopping cross section for SiO_2 on molecular basis. The energy loss value $\frac{dE}{dX}$,for 2.0 MeV He is 28.3 eV/A^o, close to the value of elemental Si-24.6 eV/A^o.(RBS) offers a powerful technique for determining directly [15-17],and with good resolution, compositional profiles in multicomponent film structures undergoing diffusion anneals. In this work, we have applied backscattering technique to study bilayer Ti based. Gold has many attractions for use as a thin-film conductor on integrated circuits [18] because of its excellent conductivity, lack of oxidation. Unfortunately the Ti/Au couple susceptible to corrosion and a barrier metal such as Pd, Pt has to be introduced [19]. The diffusion profiles for this study were measured by (BRS) using 2 MeV $^4He^+$ ions at a backscattering angle of typically 160° - 170°. The energy resolution was 3 KeV/ channel. Ti depth profiles were obtained from the RBS spectra using the RUMP simulation code [20-23]. This technique is particularly well suited to thin-film analysis as it yields a depth resolution of 100-150 A^o and is useful for thickness up to several thousand A^o. However, the lateral beam spread is ~1mm in width.

2.Experimental conditions

The films used in this study were deposited in an electron-beam evaporator in annealing pumped vacuum systeme, and examined by (RBS). Tipical deposition rates were 12 A^o /sec for Pd and Au, 9 A^o /sec for Pt and 25 A^0 /sec for Ti. Sequential evaporations were made without breaking vacuum and pressures during the evaporation did not exceed 1x 10^{-6} Torr. Annealing was carried out in two different ambiants; air and vacuum. Air anneals were performed in a standard tube furnace with constricted tube ends. Thin-film samples were radiantly heated from the back (substrate) side, while the temperature was sensed by a thermocouple attached to the front side. The interdiffusion profiles were measured using the backscattering of 1.8-2.0 MeV $^4He^+$. The apparatus has been described elsewhere [24].

3.Result and discussion

First we will present results of the experiments on the Ti/Au and Ti/Pd couples. Figure 1 shows the backscattering spectra for the scattering of 2 MeV ^{4}**He** particles from Ti/Au couple. The smooth curve shows the spectrum for the deposited films without any annealing. The methods of analyzing such spectra are given by [25-26]. The energies indicated on the abscissa are the energies for scattering from surface atoms. On annealing in vacuum at 389 ^{o}C the Ti and Au are seen to undergo rapid interdiffusion forming an alloy with calculated Au to composition ratio of 5:1 over the outermost 1000 A^{o} of the alloy. For a vacuum anneal of 490 ^{o}C at 40 min the diffusion profiles

are similar to the 389 ^{o}C anneal except that in the outermost 1000 A^{o} of the alloy the Au toTi composition ratio is 4:1.(TEM)Electron diffraction measurements of this couple showed evidence for metallic gold,TiAu4 for the 389 and 490 ^{o}C anneals the spectrum for the air anneal, fig.2,shows radically different behavior from the vacuum anneal.

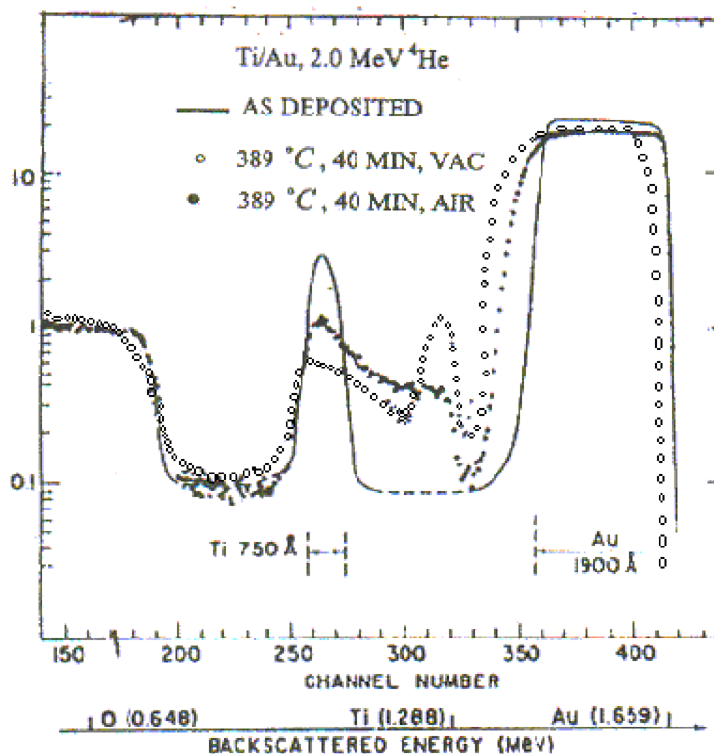

Fig.2.Backscatteing spectra from Ti/Au couples. then energy scale on the abscissa indicates backscattered energies from surface Au, Ti, and O atoms.

There is a peak corresponding to from Ti at of the alloy. this Ti is in take from of an oxide. At a lower annealing temperature,200 °C for 40 min in air, no Ti is observed in the interior of the Au films but a surface peak is observed corresponding to 4A° of Ti oxide.(Equivalents to a Ti surface density of 1.4x10 atoms cm).On annealing at312 °C for 40 min in air this surface Ti oxide peak grows to 19A° in thickness(equivalent to a Ti surface density of 7.4 x 10 atoms cm).figure 3 shows the corresponding back attiring spectra for the Ti/Pd couples. the interdiffusion under vacuum annealing conditions is less than the Ti/Au couple but when the anneal is extend to 2h the Ti and pd and are largely homogenized, similar to the Ti/Au case.

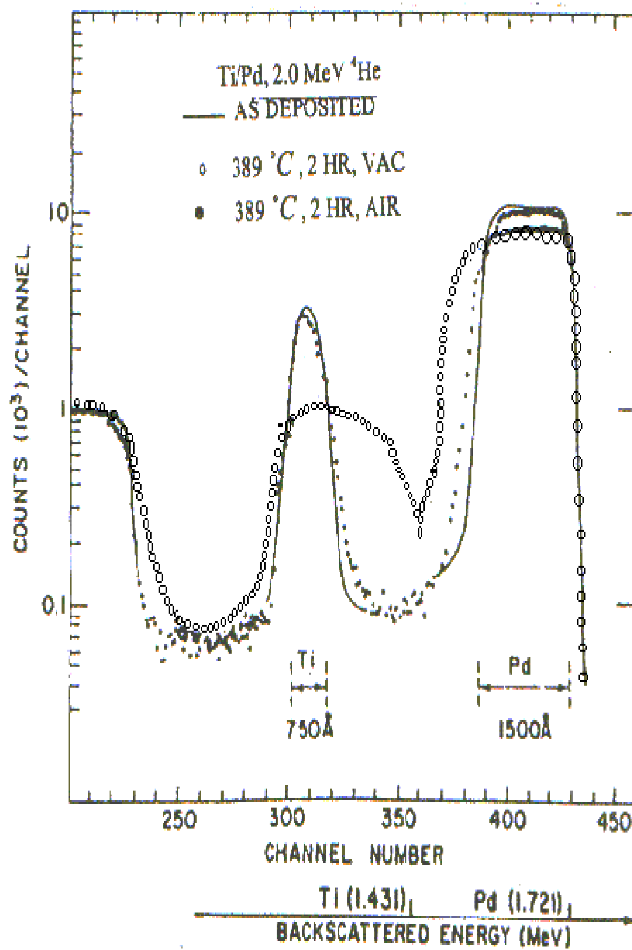

Fig.3.Backscattering spectra from Ti/pd couples

On annealing in air, however, very little interdiffusion is observed. Extending this air anneals to longer times and higher temperatures did not promote any interdiffusion beyond the interface region. the spectra for these extended anneals indicated the presence of

a substantial Ti oxide, ~100 A° in thickness, close to the Ti/pd interface. Electron diffraction (TEM) analysis of the couples diffused in vacuum did not indicate the presence of any intermediate phases. over the lower temperature range (400 ^{o}C) in which most of the anneals in the present experiments were performed, interdiffusion between the Ti and Mg films into layers structures occurred at a very low level or was unobservable interdiffusion in the Ti/Pt couples was also small for the lower temperature anneals. Equivalent air anneals for both the Ti/Mg and Ti/Pt show correspondingly small levels of interdiffusion. Spectra for Ti/Pt before and after annealing in vacuum at (490 ^{o}C) are shown in Fig. 4.

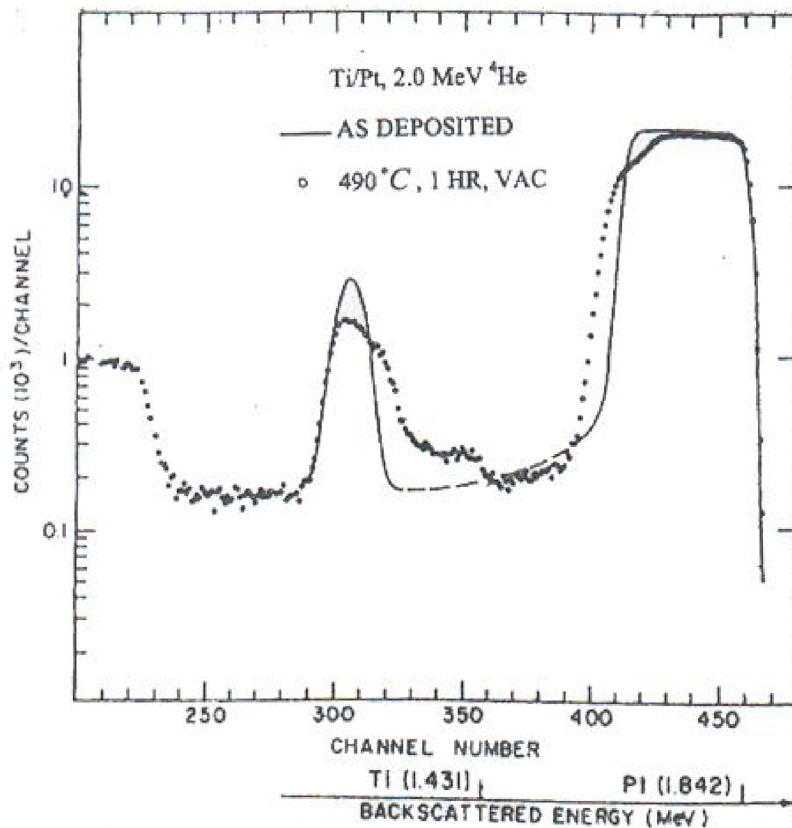

Fig.4. backscattering spectra of Ti/Pt before (line) and after (open circles) annealing at 490 ^{o}C for 1 h in vacuum.

figure 5 shows RBS spectra of Ti/Mg after annealing for 30 min at 450 °C and for 30 min at 500 °C in vacuum, respectively. spectra were also taken after annealing steps at lower and intermediate temperatures but are not shown in the figure. Up to 500 °C no reaction has occurred. After 600 °C anneal a surface layer with a Ti concentration has formed which corresponds to the $Ti_{0.5}$ $O_{0.4}$ $Mg_{0.1}$ phase. this layer is about 800 A° thick. the backscattering results for annealed Ti/Mg show little or no discernible interdiffusion between Ti and Mg for temperatures 500 °C. Interdiffusion of annealed Ti/Pd is measurable but small as shown in fig.4, the Ti reaching a concentration of ~ 10 at.% in the Pt layer after annealing for h at 490 ° C. The formation of the compounds TiPt and Ti Pd has been observed by Tisone and Drobek [24] in annealed Ti/Pt films. The experimental results that interdiffusion in the Ti-based binary systems is strongly influenced by the presence of air during annealing. The effects, however, are not identical in the various systems. In the case of Ti/Au, for example, the presence of air causes oxidation of Ti which has diffused to the surface of the Au. Surface Ti atoms are observed for annealing in air at 200 °C for 40 min. In light of spectra shown in fig. 3 for Ti/Pd and similar experiments carried out at different annealing temperatures and times, it is suggested that several processes occur simultaneously during air annealing:(I)interdiffusion of the Ti and Pd, (ii)diffusion of Oxygen through Pd and (iii)oxidation of Ti near the Ti/Pd interface.

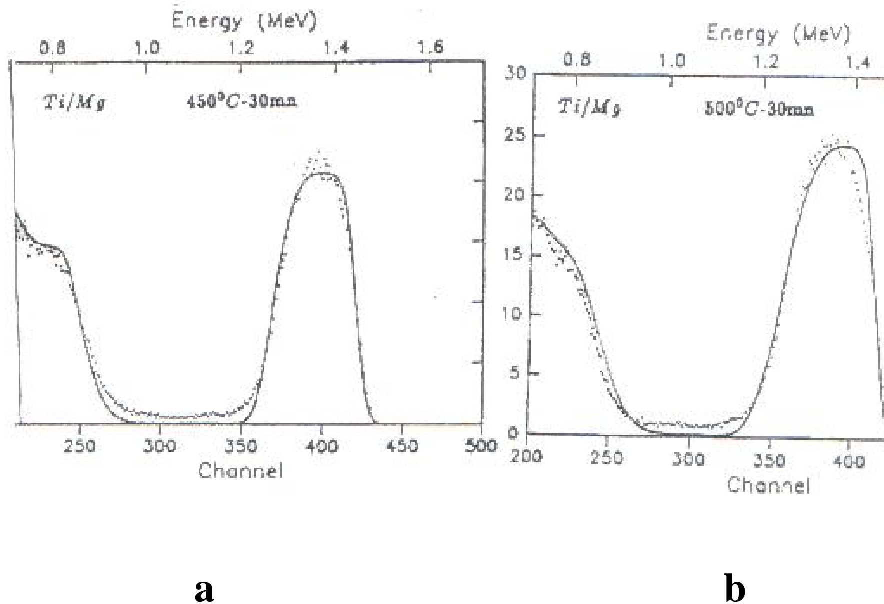

Fig.5.Backscattering spectra of Ti/Mg before (line)and after (points) annealing
(a) At450 °C for 30 min in vacuum.
(b) At 500 °C for 30 min in vacuum.

Tisone and Drobeck [24] have investigated interdiffusion in the Ti/Pd couples using transmission and glancing angle electron diffraction. They deduced the presence of intermetallic compounds from the appearance of new diffraction lines for both couples on annealing. It should be noted, how ever, that diffraction lines from the TiO_2 (rutile)phase interfere with many of those from intermetallic compounds making positive identification difficult. We can correlate the backscattering measurements with electron diffraction (TEM) to deduce that $TiAu_4$ is formed in the Ti/Au couple. However, neither backscattering (RBS)nor electron diffraction (TEM)syndicate compound formation in the Ti/Pd system. We have observed, for the case of vacuum annealing that Ti diffusion in Ti/Au or Ti/Pd couples is larger than in the Ti/Mg couple.

4.Summary and conclusions

we have investigated various couples Ti based. The Ti/Mg and Ti/Pt couples exhibit very low levels of interdiffusion for temperatures ≤500 °C. Strong ambient effects, however, are observed for the Ti/Au and Ti/Pd couples. Air annealing, as compared to vacuum, enhances diffusion in Ti/Au and inhibits diffusion in Ti/Pd. This can be explained in terms of competition between out diffusion of Ti and in diffusion of O_2 for Ti/Au, Ti diffusion through Au is sufficiently rapid that surface oxidation occurs. This surface oxidation of Ti causes continued diffusion by creating a chemical potential sink for Ti atoms at the free surface. For Ti/Pd, the in diffusion of O_2 is faster than out diffusion of so that a Ti oxide layer is formed at the interface between Ti and Pd, Ti thus inhibiting further diffusion. For Ti/Mg, the Ti diffusion was retarded by a $Ti_{o.5}\ O_{0.4}\ Mg_{0.1}$ barrier between the evaporated Ti layer and the Mg.

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