Ion beam mixing of chromium or zirconium films with sapphire

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Abstract

Ion beam mixing of thin metallic films deposited on sapphire substrates was studied for chromium or zirconium films deposited on single crystalline α - Al_2O_3 substrates. Evidence for the influence of equilibrium thermodynamic factors was sought by comparing the effects of bombarding with oxygen ions (300 and 1073 K) with those of neon ions (300 K). Thermodynamic calculations indicate that mixing might occur for Zr/sapphire at 1073 K but not at 300 K. Chromium/sapphire should not be mixed at either temperature. The implantation energy placed the peak oxygen concentration at the metal/sapphire interface in an attempt to maintain an equilibrium ratio of cations/anions and promote a radiation-induced chemical reaction across the interface. Rutherford backscattering-ion channeling measurements indicated that the widths of "mixed" regions were consistent with those predicted from ballistic considerations. Other experiments employed a heavier ion (krypton) as the mixing ion (300 K) in order to increase the mixing efficiency. Rutherford backscattering-ion channeling and x-ray photoelectron spectroscopy were used to determine the extent and nature of any interface modification. The XPS results indicated that only metallic chromium (Cr^0) was present near the interface before and after irradiation with Kr at 300 K. Zirconium exhibited only the metallic state (Zr^0) in the as-deposited film but was present as both Zr^0 and Zr^{4+} after irradiation. Some metallic aluminum (Al^0) was detected near the Zr/sapphire interface, suggesting that a local chemical reaction between Zr and the sapphire occurred during bombardment. No long-range material transport was detected for any experimental condition examined; the width of the "mixed" region in each case was consistent with that expected for ballistic effects.

Keywords: Ion Beam Mixing; Cr-Sapphire; Zr-Sapphire

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1. Introduction

Ion beam mixing relies on the kinetic nature of ion-solid interactions (ballistic mixing) and/or the disorder created at the film/substrate interface to enhance movement of atoms across the interface. In the ideal case, this mass transport removes the physically distinct interface. Early interest in ion beam mixing arose from observations that irradiation of a thin film by energetic particles sometimes increased the adhesion with the substrate [1]. In spite of many studies of the effect of ion irradiation on the adhesion, many of the underlying principles are still not understood. Sputtering of the surface by the incident ion beam often limits the maximum concentration of implanted ions that can be retained. Ion beam mixing is viewed as a technique that circumvents this limitation. Both equilibrium and nonequilibrium alloys can be prepared by this technique.

Studies of metal-metal and metal-silicon bi- and multi-layer configurations have indicated that the thermochemical properties of the film/substrate combination influence mixing phenomena. The composition and phase structure of layers formed at the interface are often those that form during thermal annealing [2-4]. The enthalpy of formation is sometimes an indicator of the probability of mixing. Mixing rates have also been linked to the mutual solubility in metal-metal couples; the solubility depends in part on the enthalpy of mixing, ΔH_m [5,6].

Differences in the amount of mixing observed in collisionally-similar but chemically-different systems implies that cascade mixing (a ballistic process) is strongly influenced by local chemical processes [6]. A model for metal-metal mixing proposed that the final distribution of the chemical species is determined by chemically-biased diffusion within a thermal spike [7-10]. This model uses the differences in ΔH_m and cohesive energies (ΔH_c) to analyze the variation in the amount of mixing for bi-layers of 4d-5d metals.

Ion-solid interactions in insulator substrates are more complex than in elemental materials. The substrate is a compound that contains at least two chemical species, usually distributed on specific sublattices. Displacement energies and efficiencies may be different for the different species. The substrate becomes metal (cation)-rich near the interface for metal/insulator combinations due to ballistic mixing processes. Chemical bond-type and electrostatic neutrality requirements may be the dominant factors in determining the final

disposition of implanted or recoiled impurity ions.

Ion beam induced mixing in systems containing an insulator either as a substrate or as a deposited film is not well-understood. Relatively few systems have been studied and the bi-layer geometry has been generally employed. Farlow et al. [11] examined a number of combinations for compliance with the "enthalpy rule". Mixing always occurred when predicted but also sometimes when not predicted.

Some of the issues involved in mixing of metal films with sapphire (single crystal Al_2O_3) substrates are addressed in this paper. The free energy of formation (ΔG) rather than the enthalpy (ΔH) is used as the thermochemical factor of interest since the entropy (ΔS) term makes a significant contribution at elevated temperatures. Using data from ref. 12, values for the reaction

were calculated to be +529.2 and +498.4 $\text{kJ}\cdot\text{mole}^{-1}$ at 300 and 1073 K, respectively, suggesting that mixing is not favored at either temperature. The reaction

yields values of +35.4 and +0.07 $\text{kJ}\cdot\text{mole}^{-1}$ at the same temperatures. On this basis, resistance to mixing should be less at 1073 K than at 300 K and much less than for the Cr/sapphire combination.

It has been suggested that implanting oxygen ions in the interface region might promote mixing. The presence of this extra oxygen (anions) might compensate for the excess metal (cations) recoiled into the substrate. If this practice is effective, mixing would be expected in the Cr/sapphire couples but not in the Zr/sapphire couples since there is total mutual solubility in the Al_2O_3 - Cr_2O_3 system at elevated temperatures, although a miscibility gap may exist below about 1100 K [13]. Limited solubility is found between Al_2O_3 and ZrO_2 .

2. Experimental procedures

The substrates were c-axis oriented, single crystal Al_2O_3 (sapphire) disks supplied with an optical-grade polish by the producer (Crystal Systems, Inc., Bedford, MA). Prior to film deposition, the substrates were annealed in flowing air at 1673 K for 120 h to remove any residual polishing damage and surface contamination. Polycrystalline thin films (50 ± 5 nm

thick) of Cr or Zr were deposited by electron beam evaporation.

In an attempt to maintain the oxygen-to-metal stoichiometry of sapphire near the interface, 45 keV O was implanted to fluences of 5×10^{16} and 1×10^{17} O·cm⁻² at 300 K in both Cr/sapphire and Zr/sapphire bi-layer samples and to 1×10^{16} O·cm⁻² at 1073 K. Another specimen of Zr/sapphire was implanted with 5×10^{16} O·cm⁻² at 1073 K. In order to separate chemical effects from ballistic effects, the results from these specimens were compared to those from samples implanted with 45 keV Ne (1×10^{17} Ne·cm⁻²) at 300 K. The energy was chosen to place the peak O or Ne concentration at the metals/substrate interface. The range (R_p) and straggling (ΔR_p) were calculated using TRIM [14].

Since the mixing efficiency is expected to increase with the mass of the mixing ion [15], other specimens were irradiated with 320 keV Kr. Both Cr/Al₂O₃ and Zr/Al₂O₃ were irradiated to fluences of 5×10^{16} and 1×10^{17} Kr·cm⁻² at 300 K.

All samples were examined using Rutherford backscattering spectroscopy (RBS) with 2.2 MeV He⁺. Spectra were taken in glancing exit angle geometry ($\theta = 40^\circ$) to enhance depth resolution.

Selected specimens from the group bombarded with Kr were analyzed using X-ray photoelectron spectroscopy (XPS). The analyses were performed in either a V. G. ESCALAB II system or a Perkin-Elmer Model 5600 ESCA unit. The base pressure was approximately 1×10^{-7} Pa. The analyzing radiation was either Mg K α X-rays (1253.6 eV) or Al K α X-rays (1486.6 eV); the analyzer pass energy was 100 eV for all analyses and the analysis area on the sample was 300 μ m in diameter. Sputter depth profiling using argon was used to establish concentration vs. depth profiles.

3. Results and discussion

3.1 Irradiation with oxygen or neon

The room temperature oxygen and neon irradiations were performed on different areas of a single sapphire disk. The samples were masked during the various steps such that each contained five areas: (a) virgin sapphire, (b) as-evaporated Cr or Zr film, (c) implanted with 5×10^{16} O·cm⁻², (d) implanted with 1×10^{17} O·cm⁻², and (e) 1×10^{17} Ne·cm⁻². Figure 1 contains the random spectra from the RBS measurements from the as-deposited Cr film and that film after implantation with 1×10^{17} O·cm⁻² and 1×10^{17} Ne·cm⁻² (45 keV). Within the

resolution of the experimental system, there is no discernible difference in the spectra. Similar conclusion are drawn from an inspection of the spectra for the a Zr/sapphire specimens treated in the same manner.

An estimate of the extent of mixing expected from a collisional model was given by the TRIM calculation of recoil density for each ion/target combination. The values are normalized to a fluence of 1×10^{17} ions·cm⁻², the highest fluence employed in this study. A cut-off value of 10^{21} recoils·cm⁻³, corresponding to about 1 atomic percent was used. The calculations for all conditions studied, summarized in Table I, show the recoil range of the Al into the Cr or Zr film to be about 3-4 nm and that of the Cr or Zr into the substrate is about 4-5 nm. These values are within the resolution of RBS for the Al-edge and the Cr or Zr peak.

These observations indicate that mixing with oxygen at room temperature gives essentially the same results as mixing with neon ions and that the extra oxygen present near the interface does not promote long-range mixing.

The RBS spectra for samples implanted with oxygen at 1073 K are given in Fig. 2 for Cr/sapphire (1×10^{16} O·cm⁻²) and in Fig. 3 for Zr/sapphire (5×10^{16} O·cm⁻²). The data for the as-deposited and the implanted regions are indistinguishable, except for a slight loss of Zr from the surface. The elevated temperature implantation of oxygen at the metal/sapphire interface evidently did not facilitate mixing beyond the ballistic process noted at room temperature.

3.2 Irradiation with krypton

In order to increase mixing efficiency, a series of samples were irradiated with 320 keV Kr to fluences of 5×10^{16} and 1×10^{17} Kr·cm⁻² at room temperature. The range of the krypton at this energy is approximately twice the metal film thickness.

Figure 4 contains the spectra for the as-deposited Cr film and a companion area implanted with 5×10^{16} Kr·cm⁻². The as-deposited spectra are best reproduced in a RUMP [16] simulation by a film thickness of 47 nm with the outermost 4 nm being oxidized to Cr₂O₃. The XPS measurements also indicated that the Cr film was oxidized to a depth less than 10 nm. The spectra indicates that some mixing occurred during ion irradiation. The RUMP simulation gives a mixed region 75 nm wide; Al is found about 5 nm into the Cr film, and Cr is found about 70 nm in the sapphire. Profiling with XPS indicated that Cr was found as

deep as 60 nm into the substrate. The TRIM calculation of recoil ranges gives values of 11 nm for Al into Cr and 62 nm for Cr into sapphire. Thus the calculation, XPS, and RBS results are consistent with ballistic mixing and the absence of long-range diffusive processes.

Chromium was detected by the XPS measurements only in the metallic state (Cr^0) at a position approximately at the interface with the sapphire substrate. Aluminum at this position was predominately in the Al^{3+} state, but there were also indications of several other oxidation states. These suboxides were also present in the spectra taken for unimplanted samples and virgin sapphire and are thought to arise from the effects of the Ar bombardment during sputter-profiling [17].

The RBS spectra for the as-deposited Zr film and the area implanted with 5×10^{16} $\text{Kr}\cdot\text{cm}^{-2}$ are contained in Fig. 5. The RUMP simulation indicates that the Zr film is oxidized to a depth of 5 nm at the outer surface and that the total thickness is 47 nm. Again, the XPS data support this conclusion. The irradiated spectra are best fit by the RUMP procedure with a mixed zone 30 nm wide; Al mixed 10 nm into the Zr, and Zr being present to 20 nm into the sapphire. These values are also consistent with the composition profile obtained by XPS depth profiling. The TRIM modeling predicts that Al will recoil 9 nm into the Zr and Zr 44 nm into the sapphire. The agreement between the RUMP fit to the experimental data and the TRIM calculations indicates that ballistic processes are the dominant means of material transport in this case.

The XPS data for the specimen implanted with 1×10^{17} $\text{Kr}\cdot\text{cm}^{-2}$ taken about 2 nm from the interface into the Zr film, shows the presence of the metallic (Zr^0) and the Zr^{4+} states as well as Al^0 and Al^{3+} . The Zr^0 and Al^{3+} states were predominant. Data taken ≈ 2 nm on the substrate side of the interface showed similar phases to be present at this position. The presence of the other states suggests that some chemical reaction between the Zr film and Al_2O_3 occurred during this high fluence irradiation. The RBS spectra-ion channeling results for this fluence indicated that the sapphire had been amorphized to a depth of about 150 nm. The chemical reaction may have occurred in this amorphous Al_2O_3 matrix. It has been reported that ion-beam-induced chemical interactions occur in amorphous SiO_2 , SiC , and Si_3N_4 after the composition is established by ballistic processes [18].

4. Summary

The extent of mixing between Cr or Zr metal films and sapphire substrates was within the amount predicted by the ballistic (recoil) model for all conditions used in this study. Room temperature irradiation with oxygen ions that came to rest near the interface gave results indistinguishable by RBS measurements from those obtained using neon ions of the same energy and fluence. Implantation of oxygen at 1073 K did not induce long-range mixing.

Using a heavier ion (Kr) to increase the mixing efficiency did not induce long-range mixing. Data from RBS and XPS measurements were consistent with the ballistic model. The Al_2O_3 substrate was amorphous after the implantations of 5×10^{16} and 1×10^{17} $\text{Kr}\cdot\text{cm}^{-2}$. The XPS measurements indicated that some of the Al near the interface had been reduced to the metallic state, Al^0 , and some Zr had been oxidized to Zr^{4+} . This local chemical reaction may have occurred in the amorphous matrix after the composition had been established by the ballistic processes.

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Figure Captions

1. RBS spectra for 50 nm Cr film/sapphire implanted with 45 keV oxygen or neon (1×10^{17} ions·cm⁻²) at 300 K.
2. RBS spectra for Cr film/sapphire implanted with 45 keV oxygen (1×10^{16} O·cm⁻²) at 1073 K.
3. RBS spectra for Zr film/sapphire implanted with 45 keV oxygen (5×10^{16} O·cm⁻²) at 1073 K.
4. RBS spectra for Cr film/sapphire implanted with 320 keV Kr (5×10^{16} Kr·cm⁻²) at 300 K.
5. RBS spectra for Zr film/sapphire implanted with 320 keV Kr (5×10^{16} Kr·cm⁻²) at 300 K.

Table I. Calculation of Recoil Ranges Using TRIM

<u>Fluence</u>	<u>Ion</u>	<u>Target</u>	<u>Energy</u> (keV)	<u>O into metal</u> (nm)	<u>Al into metal</u> (nm)	<u>Metal into sapphire</u> (nm)
1×10^{17}	O	Cr/Al ₂ O ₃	45	4	3	3.5
1×10^{17}	Ne	Cr/Al ₂ O ₃	45	6	4	5
1×10^{17}	O	Zr/Al ₂ O ₃	45	5.4	3.4	5
1×10^{17}	Ne	Zr/Al ₂ O ₃	45	5.2	3.1	4.7
5×10^{16}	Kr	Cr/Al ₂ O ₃	320	---	11	62
5×10^{16}	Kr	Zr/Al ₂ O ₃	320	---	9	44

Fig 2

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