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Final Report

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BASIC STUDIES OF ION MIXING

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OBJECTIVES

The main objective of this contract was to elucidate mechanisms of atomic mixing induced by ions with masses greater than 25 amu and energies between 50 and 500 keV. Specifically, the intent was to identify systematic trends that would reveal the nature of the main parameters that affect atomic rearrangements generated by ion irradiation. In addition, the relationship that might exist between the mechanisms of ion mixing and of thermal processing was to be explored. Metallic systems were to be emphasized.

APPROACH

→ The approach adopted was to choose samples and parameters of irradiation in such a way that the complexity of the results was minimized. The idea was that limiting cases would thereby be established for which one mechanism is dominant. Consequently, experiments at low temperatures have been pursued to investigate processes that are independent of temperature. Irradiations at elevated temperatures were employed to investigate the correlation between ion mixing and thermal processing.

In retrospect, the notion of emphasizing systematic experiments at low temperatures has served the intended purpose of this project very well. One of the main difficulties faced by ion mixing investigations at the beginning of the investigation was



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the absence of generally accepted theoretical models. This difficulty was circumvented quite effectively by using internal comparisons between results obtained on series of samples. No theory is needed to extract meaningful statements from such internal comparisons. It is this freedom from theoretical modelling that has given the results of this contract their strong impact on the field of ion mixing.

ACCOMPLISHMENTS

1. Thermal Spike Model of Ion Mixing for Transition Metal Bilayers at Low Temperature.

The single most noticeable accomplishment of this research project was the development of a phenomenological model of ion mixing observed experimentally in metal/metal bilayers at low temperatures. This model has so far been successfully tested on 27 metallic bilayer systems. The model has been a surprise to most because it is based on the concept of a thermal spike. The idea of a thermal spike is old, but had fallen in disfavor and continues to meet with some skepticism. In addition to the idea of a thermal spike, the phenomenological model of thermal spike mixing contains two other ideas that are essential to its success and that are new: (i) that the rearrangement of atoms is affected by chemical driving forces in the system, expressed by the chemical heat of mixing parameter, ΔH_m , and (ii) that the amount of intermixing also depends on the strength of atomic bonding,

expressed by the average cohesive energy, ΔH_{coh} , of the two elements in the bilayer system. The analytical form of the model is

$$2\sigma^2 = \frac{\phi K_1 \epsilon}{\rho^{5/3} \Delta H_{\text{coh}}^2} \left(1 + K_2 \frac{\Delta H_m}{\Delta H_{\text{coh}}} \right) \quad (1)$$

which states that the variance, σ^2 , of the complementary error function that describes the atomic distribution at the interface of a bilayer increases linearly with the dose of irradiation, . The constant of proportionality depends upon ΔH_m , ΔH_{coh} , the average energy deposited by the incident ion in atomic displacements per unit path length, ϵ , and the average atomic density, ρ , of the two elements of the bilayer. The model has only two adjustable constants K_1 and K_2 whose values obtained by least squares fitting are $K_1 = -0.034 \text{ A}^\circ$ and $K_2 = 27$.

2. Thermal Spike Model for Spreading of Markers in Transition Metals at Low Temperature

Systematic studies of the spreading of very thin markers imbedded in an elemental metal matrix have been undertaken to obtain clues on the specific nature of the mixing mechanisms induced by heavy ion irradiation at low temperatures. It was discovered that ion mixing systematically increases as the cohesive energy of the matrix decreases and as the energy increases that the incident

ion deposits into the displacement of matrix atoms. The amount of mixing is independent of the chemical heat of mixing between marker and host elements, or their relative masses. A correlation exists between the rate of mixing of a marker species in a host metal and the thermal diffusivity of that marker in the same host.

The sum of these marker results finds no reasonable interpretation within the binary collisions model of ion mixing, neither in magnitude or trends. They do agree qualitatively, with the hypothesis of diffusion within a thermal spike. The results have been modelled within the framework of radiation-enhanced diffusion theory, applied to the microscopic dimensions and time scales of a cascade. Experimental and calculated values of the mixing efficiencies are brought within a factor of about 2 when the mechanism of diffusion is taken to be governed by a vacancy process, but the vacancy migration enthalpy required to obtain that agreement are rather low. The conclusion is that the thermal spike model can reasonably account for atomic displacements observed with markers for ion mixing at low temperatures. Vacancy-type mechanisms for the mixing can account for the observations semiquantitatively. A positive identification of the principal mechanism has not been accomplished by these studies, however, and the task may indeed be impossible to accomplish experimentally.

3. Limitations of the Thermal Spike Model

The new question that arises out of the accomplishments described so far is where the limits of the thermal spike model lie. We have already identified one limitation very clearly; bilayers of the configuration metal/oxide do not generally follow the model described by eq. (1). A detailed study of Ti, Ni, and Cr films on SiO_2 has established that chemical driving forces remain unexpressed in these systems at temperatures below about 500°C . There appears to be a common impediment to compound formation in these systems. It is likely that a high configurational entropy penalty exists for the transition states in the chemical reaction between metal and the SiO_2 matrix. A large activation energy could suppress specific chemical effects at low temperatures if the process is dominated by distortion of the SiO_2 matrix. A strong temperature dependence is apparent at high temperatures. It remains an open question how and when the metal-specific chemistry enters into play and determines the final phase formation.

Another aspect that has been considered is that of microstructure. It is not known if and how the microstructural makeup of a bilayer affects the outcome of ion beam mixing in the thermal spike regime. A first attempt has been undertaken to probe this question, but the result is as yet inconclusive. We have, however, identified a possible approach.

4. Ion Mixing of Metal/Si Bilayers

Several aspects that are particular to metal/Si systems have been clarified. It was long known that when a Cr/Si bilayer reacts thermally, an interfacial CrSi_2 layer forms. The growth of this layer is reaction-limited (as opposed to transport-limited), but the seat of the rate-limiting reaction was unknown. We have shown by ion mixing experiments that it is the Cr/ CrSi_2 interface that limits the reaction.

We have also shown that when a metal/Si reaction proceeds via ion mixing, the dominant moving species is not always the same as that observed for thermal annealing. For example, in Ni_2Si and Pb_2Si only the metal moves in a thermal reaction, but both species do during ion mixing. In CrSi_2 , only Si moves in both instances. Generalizing on the basis of other known correlations, this means that for refractory transition-metal disilicides, the dominant atomic transport processes in ion mixing and thermal annealing are probably similar, but that they are not for near-noble dimetal silicides.

5. Thermal Reaction of Bilayers

The processes in thermal reactions of metallic bilayers have been investigated in parallel with ion mixing experiments.

Reactions involving Al have been considered in particular. We have made the first measurements of thermal reaction rates of

transition metal films with Al substrates and found that Ti, Ni, and Pt all react by a transport-limited (annealing duration)^{1/2}-type law. To accomplish these measurements, extreme care is required to avoid native oxide layers and grain boundary effects. We thus first developed a technique to grow Al sheets with cm-sized grains as substrates and in situ sputter-cleaning of the Al surface immediately prior to depositing the metal film. It was also necessary to develop a novel diagnostic technique to determine the residual oxygen contamination at the interface between the metal film and the Al substrate with which monolayer sensitivities are reached. The following facts were established:

- Al grain boundaries lead to laterally non-uniform reaction fronts (between the growing Al_3Ni film) and the Al interface. By contrast, the planarity of the growing layer for Pt (which forms Al_3Pt_2) and Ti (which forms Al_3Ti) is unaffected by Al grain boundaries.
- Contamination such as oxygen, can alter the reaction process greatly. Volume concentration of less than 1 at % in the Ni film substantially reduce the reaction rate; interfacial contaminations of the size of the native oxide of Al (3.5 nm) suffice to stop the reaction completely.
- For the Ti/Al reaction, oxygen at the sample surface or at the interface suppresses the nucleation of the Al_3Ti compound.
- The location of least oxygen content determines where the compound nucleates and grows.

The implications of these facts on the ion mixing of Al with

transition metal films remain largely unexplored. A first study of the mixing of Ni, Mo and Pt films with Al near 77K suggests that the thermal spike model applies in these cases too, but our latest results have shown that with films of the lightest transition metals, the model breaks down.

A major contribution was made to the subject of amorphous metallic compound formation after W.L. Johnson had discovered that thermal annealing of metallic bilayers can lead to the growth of an amorphous interfacial compound layer. We confirmed experimentally that in each of the cases considered, only one species moves, as had been conjectured. That rule has subsequently been verified by others in different systems.

6. Outlook

Our studies of ion mixing were based on irradiations with heavy ions in the 100-500keV energy range and analysis by backscattering spectrometry. This approach has been rewarding in terms of the deepened understanding of the ion-solid interaction that has resulted. One insight gleaned at the conclusion of this program is that thermal spikes, when they develop, are initiated only at the very end of a cascade, when displaced atoms are falling in the energy range of less than 1 keV. There is, hence, no need to start with very high energy beams if the purpose is to generate efficient atomic mixing by thermal spikes. The benefits of our research carried out at the 100 keV range thus extends

down to the energy range of keV. This is the range where practical ion beam processes (sputtering, ion etching, plasma techniques) are used to deposit and to pattern films and substrates. Each increase in the fundamental understanding of these processes can have major practical benefits. Our approach to ion mixing has shown its merits: by raising the energy to 100's of keV, the affected depth of the sample is expanded sufficiently to make analysis possible with tools that need not have monolayer resolution in ultra high vacuum ambients. The pace of progress is correspondingly brisk. It is clear that ion mixing studies in the 100 keV energy range are rewarding scientifically and practically very relevant. It is our desire to extend them. We are looking for sources of support to continue this work.

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