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STIMULATION OF AMORPHOUS LAYERS IN THE CO-SI SYSTEM BY THIRD ELEMENT ADDITIONS

Denise Brandt

Introduction

Multilayer thin films play an important role in our technology today. They can be found in many devices such as magnetic hard disks, microelectronic circuits, and x-ray optical elements. In many of these metal-metal and metal-metalloid multilayers, amorphous layers have been discovered using various techniques such as extended x-ray absorption fine structure (EXAFS) and high resolution transmission electron microscopy (HTEM). These amorphous layers enhance the magnetic and electrical properties of the alloy. They also affect the mechanical and structural properties of the system.

The solid state amorphous reactions (SSAR) occur whether the layers are formed by epitaxy or by sputtering. The amorphous phase occurs if there is a large negative heat of mixing between the initial components.¹ This indicates that it requires less energy for the amorphous phase to form than for the crystalline phases to form. The reaction is also limited by diffusion rates. In order for the amorphous phase to form, one of the components must have a much larger diffusion rate in the intermixed layer between the components.^{1,2}

Although SSAR is a very active research subject, no studies have explored the possibility that the formation of amorphous layers might be promoted by adding a third element to the layers. To be effective, the third element should lower the free energy of the system and promote faster diffusion of the mobile component in the system. Research is currently being done on this idea. In this paper, the first stages of this research will be discussed. The research is being conducted on the Co-Si system. The Co-Si system is similar to the Ni-Si system but while the Ni-Si system forms amorphous layers the Co-Si system does not. Ti and Rh are to be used as the third elements in the system. The samples are made by two different sputtering techniques. This will show the effect of the quality of vacuum on the amorphous reaction.

The Co-Si System

Nickel and cobalt have lattice parameters that are within 2% of each other, their atomic sizes are within 1%, their melting points are within 50 C, they are both the mobile element during silicide formation, and they form similar phases with Si. Therefore, one may expect the systems to react similarly under the same conditions. However, this is not the case when thin films of the two systems are formed. The Ni-Si system forms amorphous layers that grow during the annealing process.

In the Co-Si system interlayers of 4.5 nm thickness are formed. The interlayers are mostly amorphous with a small amount of compound crystallites, which are unaffected by annealing at 250 C. Annealing at 300 C produces a mostly crystalline microstructure.² From previous experiments it has been determined that nickel-silicon reactions occur approximately 10^5 times more rapidly than cobalt-silicon reactions. This implies that by increasing the reaction rate of Co-Si reactions, amorphous layers might be produced. The reaction time can be increased by reducing the heat of mixing or by increasing the diffusion rate. The addition of a third element may increase the reaction rate.

Third Element

By examining free energies of mixing and relative sizes of atoms in comparison with Co and Si, educated guesses were made of third element additions that might alter the diffusion factor or the thermodynamic factor independently. Ti and Rh respectively, were selected for the Co-Si system based on the above criteria and experimental convenience.

The diffusion factor was estimated using an empirical equation developed by Bernardini³ that predicts the diffusion behavior of impurity elements in the grain boundaries of binary alloys. The equation was developed from an equation of grain boundary energy and theories on adsorption. The addition of solute B to A affects the grain boundary self-diffusion of A according to the formula:

$$D_b^{AB/A} = D_b^{A/A}(1 + (b_v^{AB/A} - 2 s^B)c^B).$$

Where $D_b^{AB/A}$ is the boundary diffusion coefficient of A in AB, $D_b^{A/A}$ is the self diffusion coefficient of A along the grain boundaries, $b_v^{AB/A}$ is the temperature dependent coefficient for the effect of solute B on the lattice self-diffusion of A, s^B is the ratio of solute concentrations in the boundary and in the lattice, and c^B is the bulk concentration of B. This equation suggests that solutes having small s^B values and large b_v values have been established for few combinations of elements, so they must be estimated more indirectly from heats of solution⁴ and other empirical correlations.⁵

These estimates led to the choices of Ti and Rh. For Ti, b_v is large, which indicates that it will speed up the diffusion of the Co, which is the rate controlling step in the Co-Si system. Its s^B value is also large, but not large enough to overcome the effect of b_v . Thermodynamically, Ti behaves similarly to Si, so Ti should exert its effect mainly on the diffusion factor. On the other hand, for Rh, b_v is unknown and s^B is small, which indicates that it will not segregate appreciably. Accordingly, rh would be a suit third element to examine the effect of the thermodynamic factor in the Co-Si system.

Sample Preparation

Co-Si layers were formed by sputtering instead of epitaxy because sputtering requires less of a vacuum, it produces larger grains which should minimize the effects of grain boundary diffusion within the layers, and it is faster and cheaper than epitaxy. The sputtering was performed on two different types of sputtering machines. 100 nm and 50 nm layers were made on a (100) Si wafer about 1 in square on a high vacuum sputtering machine at the National Nanofabrication Facility at Cornell University. Similar samples are to be made on a table top sputtering machine that is normally used to sputter gold and palladium on SEM specimens.

The samples from the table top sputterer will consist of one layer of sputtered Co on a silicon wafer and a second silicon wafer similarly coated and inverted on top of the cobalt layer. These layers are not bonded very well to the Si and therefore will be annealed under pressure in hydrogen at 300 C for a short time to improve the bonding. The samples will then be cut to approximate TEM specimen size before the anneal so that they will later fit in the specimen holder. Once the layers are bonded the specimens are ready for the addition of the third element.

The third element will be deposited from an aqueous solution on to the faces perpendicular to the layers before being annealed. After the anneal, TEM specimens will be prepared for inspection of the extent of penetration of third element along the layers and changes in the extent of intermixing.

Holding Device

The holding device required for the first anneal of the samples made from the tabletop sputtering machine had to be designed. To promote the bonding of the layers in these samples, the first anneal must occur under pressure. The final design is shown in Figure 1.

The pressure was accomplished by using two different alloys with two entirely different coefficients of linear expansion. From the expansion coefficient and the annealing temperature, the strain in the materials can be determined using

$$e = a\Delta T$$

and the effective strain determined from:

$$e_{\text{effective}} = e_{\text{screw}} - e_{\text{tube}}$$

Then the stress in the screw can be determined by

$$\sigma = eE.$$

Using Invar for the tube and 316 stainless steel for the screw, a pressure of approximately 135 ksi would be reached in the screw at 300 C and thus in the sample. The actual pressure should be smaller because the coefficient of expansion reduces at higher temperatures for the stainless steel while the coefficient for invar remains constant for this temperature range. Using

$$\sigma = F/A$$

the stress in the tube can be determined. For the dimensions shown in Figure 1, the pressure in the tube is only 2.9 ksi.

The tensile and compressive strengths of these materials must also be taken into consideration. The Invar has a strength of approximately 72 ksi which is well above the pressures applied and is not of concern. However, the screw must withstand much higher pressures. The 316 stainless steel when cold rolled achieves tensile strengths of 100 to 150 ksi and yield strengths up to 135 ksi. These high strengths should support the pressure produced by the temperature with little plastic deformation occurring. Many alloys would lose their increased strength from cold work at 300 C but for steels the recrystallization temperatures are much higher and they can maintain high strength at this temperature.

Precautions must be taken to ensure that the threaded portions of the device do not strip under pressure. The minimum length of thread contact can be determined by the following equation:⁶

$$L_e = 2A_t / [3.1416K_n \max [1/2 + .57735n(E_s \min - K_n \max)]]).$$

The above equation is valid for threads of the same material. The values needed for calculations can be found on the attached table.⁶ If the threads are of two different materials, the following calculation must be done:

$$J = \frac{A_s \times \text{tensile strength of external thread material}}{A_n \times \text{tensile strength of internal thread material}}$$

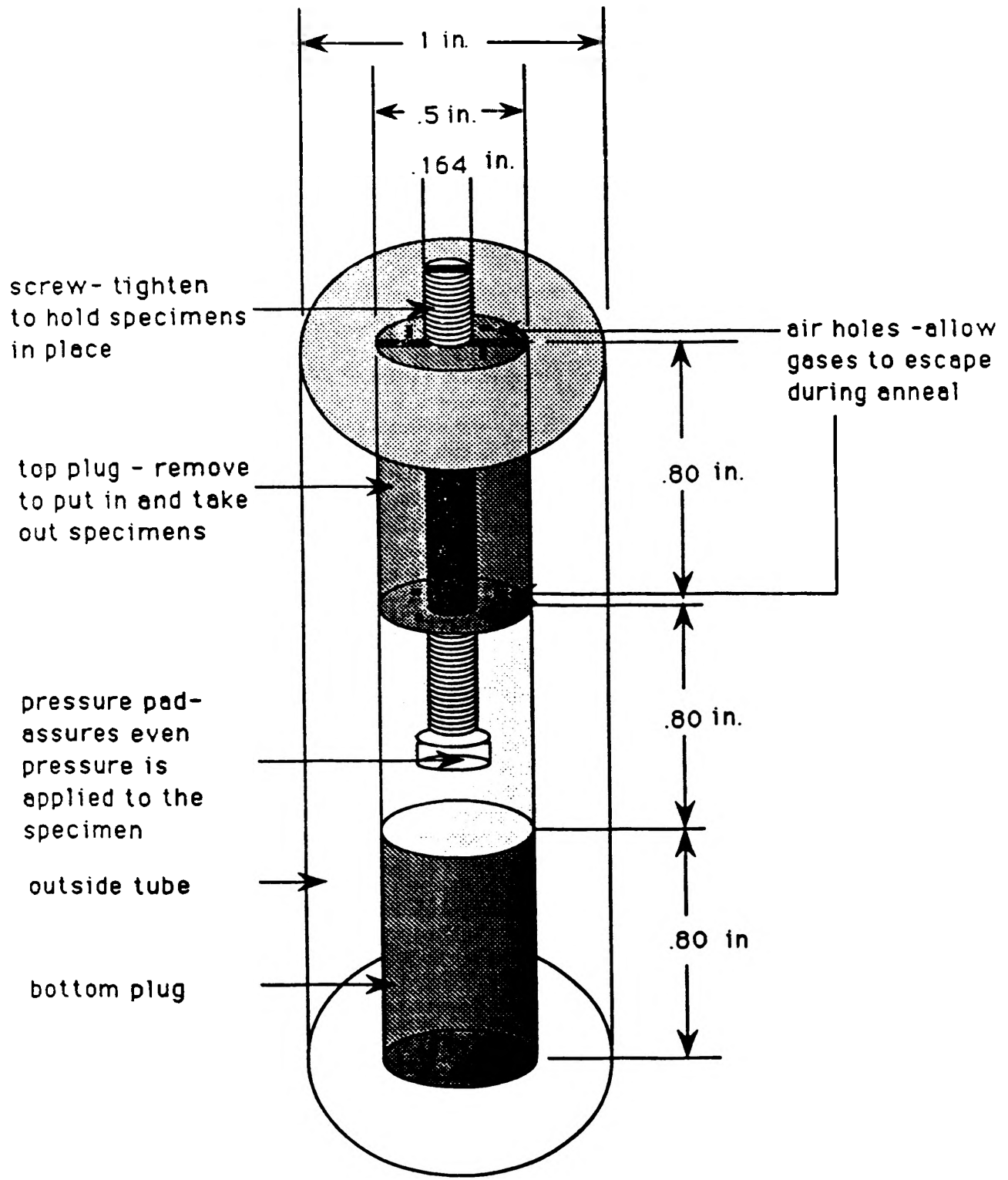


Figure 1. holding device

Table 3b. Fine-Thread Series, UNF and UNRF — Basic Dimensions

Sizes No. or Inches	Basic Major Diam., D	Thds per Inch. n	Basic Pitch Diam., ^a E	Minor Diameter		Lead Angle A at Basic P.D.	Area of Minor Diam. at D-2n ^b	Tensile Stress Area ^c
				Ext. Thds., A ₁ (Ref.)	Int. Thds., A ₂			
				Inches	Inches			
0 (.060)	0.0600	80	0.0519	0.0451	0.0465	4 23	0.00151	0.00136
1 (.0731) [*]	0.0730	72	0.0640	0.0565	0.0580	3 57	0.00237	0.00228
2 (.086)	0.0860	64	0.0759	0.0674	0.0691	3 45	0.00339	0.00332
3 (.099) [*]	0.0990	56	0.0874	0.0778	0.0797	3 43	0.00451	0.00452
4 (.112)	0.1120	48	0.0985	0.0871	0.0894	3 51	0.00576	0.00581
5 (.125)	0.1250	44	0.1102	0.0979	0.1004	3 45	0.00716	0.00730
6 (.138)	0.1380	40	0.1218	0.1082	0.1109	3 44	0.00874	0.00904
8 (.164)	0.1640	36	0.1460	0.1309	0.1339	3 28	0.01285	0.01374
10 (.190)	0.1900	32	0.1697	0.1528	0.1562	3 21	0.0176	0.0200
12 (.216) [*]	0.2160	28	0.1928	0.1734	0.1773	3 22	0.0226	0.0258
1/4	0.2500	28	0.2268	0.2074	0.2113	2 52	0.0326	0.0352
3/16	0.3125	24	0.2854	0.2629	0.2674	2 40	0.0524	0.0551
1/2	0.3750	24	0.3479	0.3254	0.3299	2 11	0.0809	0.0858
7/16	0.4375	20	0.4050	0.3780	0.3834	2 15	0.1099	0.1157
1/2	0.5000	20	0.4675	0.4405	0.4459	1 57	0.1489	0.1569
9/16	0.5625	18	0.5264	0.4964	0.5024	1 55	0.189	0.202
5/8	0.6250	18	0.5889	0.5589	0.5649	1 43	0.241	0.256
3/4	0.7500	16	0.7094	0.6763	0.6823	1 30	0.351	0.373
7/8	0.8750	14	0.8286	0.7900	0.7977	1 24	0.489	0.519
1	1.0000	12	0.9459	0.9001	0.9098	1 36	0.625	0.663
1 1/8	1.1250	12	1.0709	1.0258	1.0348	1 28	0.812	0.856
1 1/2	1.2500	12	1.1959	1.1508	1.1598	1 16	1.024	1.073
1 3/8	1.3750	12	1.3209	1.2758	1.2848	1 9	1.260	1.318
1 1/2	1.5000	12	1.4459	1.4008	1.4098	1 3	1.521	1.581

^a Secondary sizes.
^b British Effective Diameter.
^c See formula, page 1279.
 Design form for UNF threads. (See figure on page 1281.)
^d Basic minor diameter.

where

$$A_s = 3.1416nL_e K_{n \max} [1/(2n) + .57735(E_{s \min} - K_{n \max})] \text{ and}$$

$$A_n = 3.1416nL_e D_{s \min} [1/(2n) + .57735(D_{s \min} - E_{n \max})].$$

If J is greater than 1, then

$$Q = JL_e$$

where Q is the length of thread engagement required to prevent stripping. For the holding device the length of the thread contact was calculated to be .758 in for a size 8 screw with a thin thread series. To have a small safety factor we made a contact length of .800 in.

At the annealing temperature under pressure the threads will have a tendency to weld together. A boron nitride spray is sprayed on to the threads before the anneal to prevent this problem. The boron nitride contains additives that will allow it to stick to the metal and form a protective coating that remains at high temperatures.

One end of the screw is rounded to about a 3/8 in radius. A metal pad is placed on the rounded end. The pad can then move to assure even distribution of pressure on the specimens. The screw is tightened just enough to hold the specimens in place. The actual pressure is applied gradually with the temperature change before the anneal.

Continuing Research

This project is being carried on by another student next semester. This student will make the samples in the tabletop sputter, anneal them, anneal all of the samples with third elements, prepare TEM specimens from these samples, view them with the TEM, and determine the results.

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