Economical Sputtering System To Produce Large-Size Composition-Spread Libraries Having Linear and Orthogonal Stoichiometry Variations

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A multitarget sputtering machine with a water-cooled rotating substrate table has been modified to produce films on 75 mm × 75 mm wafers which map large portions of ternary phase diagrams. The system is unconventional because the stoichiometries of the elements sputtered on the wafer vary linearly with position and in an orthogonal manner. Subsequent screening of film properties is therefore quite intuitive, since the compositional variations are simple. Depositions are made under continuous rotation, so either intimate mixing of the elements (fast rotation) or artificial layered structures (slow rotation) can be produced. Rotating subtables mounted on the main rotating table hold the 75 mm × 75 mm substrates. Stationary mask openings over the targets and mechanical actuators that rotate the subtables in a precise manner accomplish the linear and orthogonal stoichiometry variations. Deposition of a film spanning the range $SiSn_xAl_y$ ($0 < x, y < 1$), with Sn content increasing parallel to one edge on the wafer and Al content increasing in a perpendicular direction, is given to illustrate the effectiveness of the method. Since the system was easily and inexpensively built, it has enabled our research program in combinatorial materials synthesis to begin without large scale funding.

Introduction

Physical vapor deposition has long been used to prepare stoichiometric ranges of compounds or to explore phase diagrams using the so-called composition-spread approach.[1−4] In this method a large range of stoichiometries of binary, ternary, or quaternary systems is made on a single substrate in a single deposition run. In such an approach, the substrate is generally covered by a continuous film rather than individual isolated pixels of material, as is common in combinatorial materials science.[5]

In one of the first reports of composition-spread methods, Kennedy et al. produced isothermal ternary phase diagrams using three evaporation sources opposite the vertexes of a triangular substrate.[1] Hanak[2] showed how a multicomponent single target could be used to deposit a spread of compositions on a single substrate. Van Dover et al. used up to four pure targets placed on the corners of a square.[3] The targets are energized simultaneously. They obtain a spread of materials on the substrate where the beams from the targets overlap. Although these three methods are simple, with no moving parts in the deposition chamber, they do not lead to films where the composition varies in a simple linear fashion with position on the substrate. However, they do ensure intimate mixing of the target materials because the deposition is simultaneous.

Xiang and co-workers[4,5] have developed a system whereby linear composition variation with position is possible. In this method, a target is energized and then a shutter moves slowly across in front of the substrate, blocking the beam as it passes. As a result, the thickness of a particular element or compound varies linearly with position.[4] Then the substrate is rotated and moved under a different target and the process is repeated to get a linearly varying thickness of a second element or compound in a different direction (either at 120° or at 90° to the first direction). The process can be repeated many times to build up complex overall stoichiometries. However, the film must be heat-treated to cause interdiffusion and the formation of homogeneous phases from the discrete layers. A number of motors within the vacuum chamber are required to drive the precise shutters, which move only 20 μm above the substrate surface.[4]

It was our goal to build a system for composition-spread studies of amorphous binary, ternary, and quaternary metal systems. We wanted to ensure intimate mixing of the elements as sputtered, because any heating step to cause interdiffusion of thick layers would crystallize the amorphous phases. We wanted to ensure linear and orthogonal composition variations so that stoichiometries could be determined simply from the position on the substrate. Film thicknesses of up to 5 μm were desired. The system had to be inexpensive and

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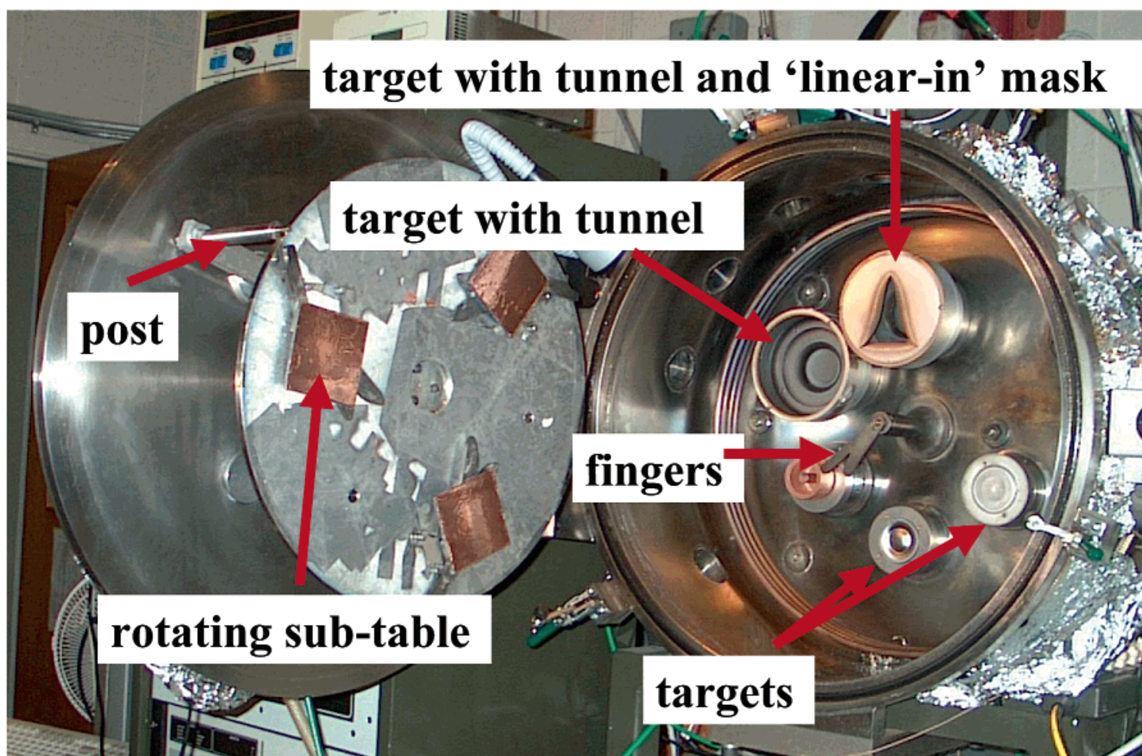

Figure 1. Photo of the sputtering machine with the two-axis combinatorial table in place. Certain features of the machine are labeled as indicated.

an "add-on" to an existing multitarget sputtering machine. Finally, we wanted large substrates (75 mm × 75 mm) to maximize the number of patterned electrodes with connecting leads that could ultimately be fabricated for combinatorial electrochemistry. In this paper, we describe the novel system that we designed and built to accomplish these goals.

Description of the Sputtering Method

The sputtering machine that we use is a Corona Vacuum Coaters (Vancouver, BC, Canada) model V-3T system. It has an 18 in. diameter cylindrical vacuum chamber, a rotating water-cooled substrate table (16 in. diameter), up to five magnetrons, and a plasma-cleaning electrode. There is one RF power supply and there are 3 DC magnetron power supplies. The system is turbo pumped and also has a R2000 series Polycold fast cycle water vapor cryopump to eliminate water vapor. The axis of the rotating table is horizontal, and the faces of the sputtering targets are vertical. A picture of the machine is shown in Figure 1.

The sputtering targets are 5.0 cm in diameter, and the target to substrate distance is 5 cm. The magnetrons are placed at 60° increments on the flat back wall of the chamber. The centers of the targets are 13.3 cm from the cylindrical axis of the chamber. The rotating substrate table shares the same cylindrical axis.

Figure 2a shows the mass deposited as a function of position on the substrate (passing under the center of a target) when the substrate table is stationary. The data points were collected by weighing 1.3 cm diameter pieces cut from the film with a precision punch. The measurements were made with a Cahn 29 microbalance. The deposited mass is largest directly under the center of the target, as expected. The mass decreases away from

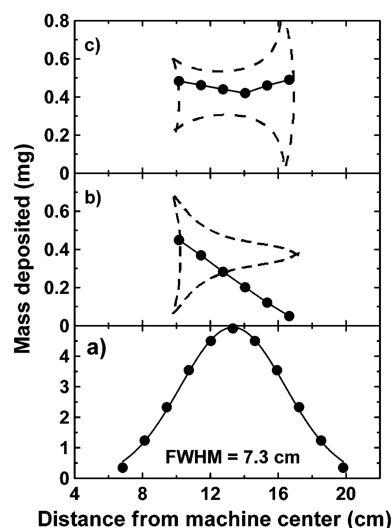

Figure 2. (a) Mass deposited on a 1.3 cm diameter disk as a function of position from the center of the axis of the stationary substrate table. The axis of the sputtering target is at 13.3 cm. The solid line is a Guassian best-fit to the data. (b) Mass deposited on a 1.3 cm disk as a function of position, when sputtering was done on the rotating table through the "linear in" mask opening. The dashed line is a scale depiction of the mask opening. (c) Mass deposited on a 1.3 cm disk as a function of position, when sputtering was made on the rotating table through the "constant" mask opening. The dashed line is a scale depiction of the mask opening.

the target axis (at 13.3 cm) and approximately follows a Gaussian, as shown by the solid curve.

Consider what would happen if a single target were energized and the table rotated. A "doughnut"-shaped band would be deposited on the entire substrate table. From Figure 2, the band would be thickest at a location 13.3 cm from the center of the "doughnut". The thick-

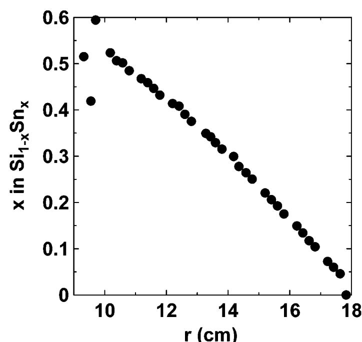

Figure 3. Composition of the $SiSn_x$ film versus position. The film was made using the "constant" mask opening opposite to the Si target and the "linear in" mask opening opposite to the Sn target. The substrate table was rotating at 30 rpm during deposition.

ness of the deposit would fall off at both larger and smaller radii. It was our goal to make a deposit whose thickness or mass per unit area varies linearly with radius, as shown in Figure 2b. This was accomplished by placing a mask opening over the target whose shape is given by the dashed line in Figure 2b. The profile of the opening was calculated by considering the Gaussian beam profile and the fact that the deposit at radius r is spread over a circle of circumference $2\pi r$.

Our targets have a 4 in. diameter tunnel attached to the outside of their ground shields. The tunnel is about 4.5 cm long, and the mask opening is attached to the front of the tunnel. The distance between the mask opening and the substrate table can be adjusted between 1 and 5 mm. The data points in Figure 2b show the mass of 1.3 cm diameter disks of a Sn film deposited through the mask opening shown. The mass versus radius varies linearly. We call this mask opening a "linear in" opening.

Other mask openings can be made to define any desired thickness versus radius profile. For example, the mask opening shown by the dashed curve in Figure 2c was designed to give a constant thickness or mass per unit area versus radius. The data points in Figure 2c were collected for the sputtering of Mo through the mask opening shown. The profile is roughly constant. We call this mask opening a "constant" opening.

The mask openings shown in Figure 2b and c have been used to prepare the binary systems $MoSn_x$ ($0 < x < 1$)[6] and $SiSn_x$ ($0 < x < 1$).[7] In these cases, a "constant" opening was placed over the Mo or Si targets and a "linear in" opening was placed over the Sn target. Figure 3 shows electron microprobe results for the composition of the $SiSn_x$ film as a function of radius. The stoichiometry variation is approximately linear.

To produce linear and orthogonal variations of two elements or compounds, we use a modified substrate table that incorporates three rotating subtables. The same "constant", "linear in", and "linear out" masks are used over the target tunnels. Figure 4 shows a schematic of the modified substrate table and its operation. The figure shows the substrate table as viewed from the back of the sputtering chamber. Each of the parts (a, b, and so forth) represents a "snapshot" of *only one* of the subtables at a moment of time. We illustrate the operation of the system with a description of the production of $SiSn_xAl_y$ ($0 < x, y < 1$).

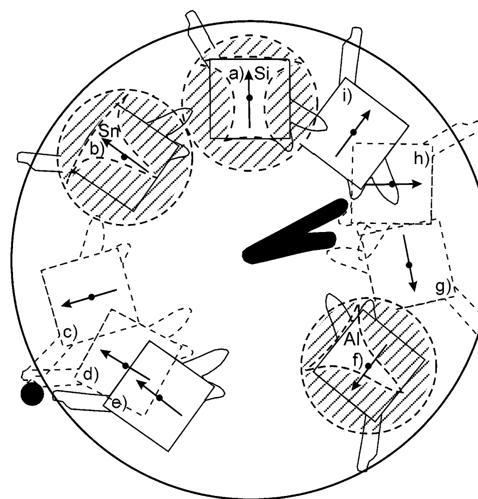

Figure 4. Schematic diagram of the rotating table showing "snapshots" of one subtable at various instants in time. The sequence a–i is described in the text.

Figure 4a shows the subtable positioned opposite the Si target which is covered with the "constant" mask opening. The arrow on the subtable is a guide to mark its orientation. This ensures that a layer of Si that is uniform in thickness is deposited over the 75 mm × 75 mm square subtable. The main table always rotates continuously, and at the moment in time corresponding to Figure 4b, the subtable is positioned opposite the Sn target which is covered with a "linear out" mask opening. This ensures that a layer of Sn that varies linearly in thickness in the radial direction (*parallel to the arrow*) is deposited on the 75 mm × 75 mm subtable. The main table rotates continuously, and at the time corresponding to Figure 4c, an actuator arm connected to the subtable strikes a post that is fixed to the chamber. This causes the rotation of the subtable on its bearing as shown in Figure 4c–e, until it is in a position where the arrow on the subtable is pointing tangentially to the edge of the main table (Figure 4e).

The main table rotates continuously, and at the time corresponding to Figure 4f, it is located opposite to the Al target which is covered with the "linear in" mask opening. This ensures that a layer of Al that varies linearly in thickness in *a direction perpendicular to the arrow* is deposited on the 75 mm × 75 mm subtable.

The main table rotates continuously, and at the time corresponding to Figure 4g, a second actuator arm strikes a fixed pair of "fingers" that are rigidly attached to the chamber. This causes the rotation of the subtable on its bearing as shown in Figure 4g–i back to its original orientation with respect to the main table, with the arrow pointing in a radial direction. The subtable then returns to the position depicted in Figure 4a, and the process repeats. Typically, we rotate the main table at about 20 revolutions per minute, so each of the three subtables passes under each target 20 times per minute. Of course, this is fully adjustable. Should one want to prepare multilayers, one would decrease the angular velocity.

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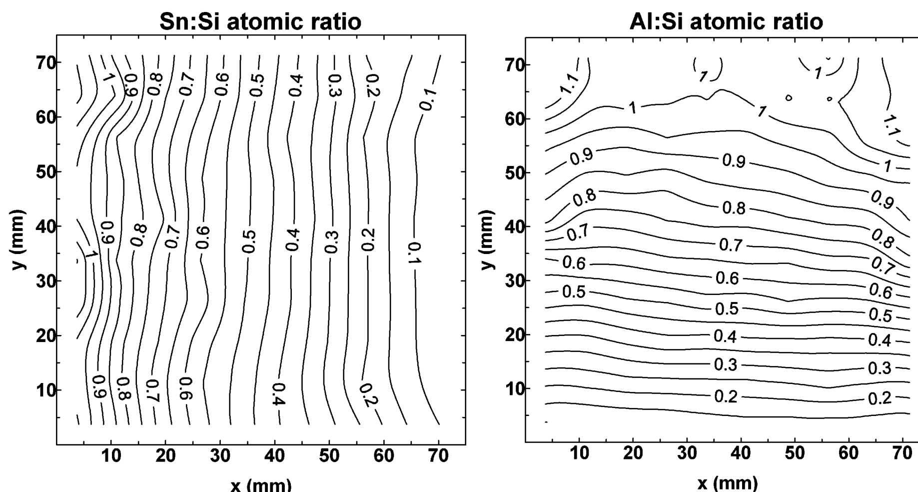

Figure 5. Contour maps of the Sn/Si and Al/Si atomic ratios versus position on the 75 mm × 75 mm $SiSn_xAl_y$ film. The film was made using the apparatus depicted in Figure 4.

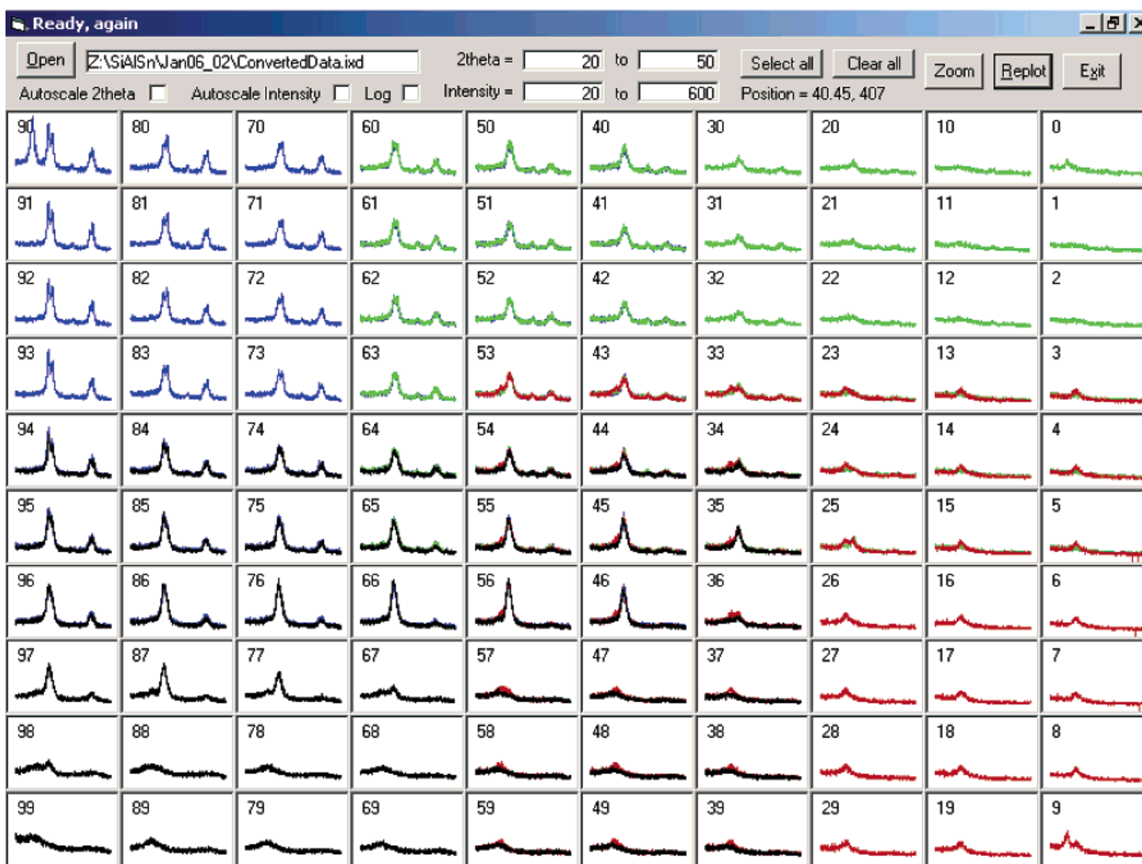

Figure 6. X-ray map produced for a $SiSn_xAl_y$ film made using the apparatus in Figure 4. The position of each pattern in the figure matches its position from the film. The range of scattering angle displayed in each panel is from 20 to 50°. The pattern in the top left corner (scan 90) was taken with the X-ray beam partially off the sample, so a broad peak from the mounting tape is observed below 30°. In many of the other patterns, diffraction peaks from tin (the 200 peak at 30.65°, the 101 peak at 32.019°, the 220 peak at 43.87°, and the 211 peak at 44.90°) and aluminum (the 111 peak at 38.47° and the 200 peak at 44.74°) are observed. Amorphous regions are observed over a good portion of the film, for example in the bottom two rows and rightmost two columns.

To illustrate the performance of the system, we prepared three 75 mm by 75 mm films of $SiSn_xAl_y$ ($0 < x, y < 1$). The sputtering powers used were 200 W rf for Si, 30 W dc for Al, and 13 W dc for Sn. The argon pressure was about 4 mTorr during deposition. The deposition proceeded for about 8 h, after which the film was about 1 μm thick in its thickest location. On one subtable, we mounted a 75 mm × 75 mm copper foil substrate, on another we mounted a 75 mm × 75 mm cleaved Si wafer (111 orientation), and on the third subtable we mounted twenty-five 1.3 cm diameter preweighed Cu foil disks. The film deposited on the Cu foil was used for electron microprobe analysis; the film on the Si wafer was used for X-ray diffraction; and the disks were used to obtain the sputtered mass per unit area as a function of position on the subtable.

Figure 5 shows a contour map of the Sn/Si and Al/Si atomic ratios measured by electron microprobe plotted versus position on the 75 × 75 mm wafer. One hundred data points were collected on a 10 × 10 grid with a spacing of 7.5 mm between data points. It can be clearly seen that the amounts of Sn and Si in the film increase approximately linearly and orthogonally.

X-ray diffraction measurements were performed using an INEL CPS120 curved, position sensitive detector coupled to an X-ray generator equipped with a Cu target X-ray tube. There is a monochromator in the incident beam path that limits the wavelengths striking the sample to Cu Kα. The incident angle of the beam with respect to the sample is about 6°, which does not satisfy the Bragg condition for the Si(111) wafer used as a substrate. The wafer therefore acts as a "zero background holder". The detector measures the entire diffraction pattern between the scattering angles 6° and 120° at once. Typical measurement times are 5 min per point. The film sample is placed on an $x-y$ translating stage that allows measurement and move operations to be sequentially programmed. Typically, the wafer was scanned in a 10 × 10 square grid with 7.5 mm between points. Figure 6 shows an X-ray map of the $SiSn_xAl_y$ film produced with software developed in-house. In the figure, the position of each pattern matches its position on the wafer. The tin content of the film increases from right to left, and the aluminum content increases from bottom to top. From the figure it is easy to see the large amorphous range of the film obtained under these conditions.

Conclusions

A multitarget sputtering machine with a water-cooled rotating substrate table was modified to produce films on 75 mm × 75 mm wafers which map large portions of ternary phase diagrams. The stoichiometries of the elements sputtered on the wafer vary linearly with position and in an orthogonal manner. Rotating subtables mounted on the main rotating table hold the 75 mm × 75 mm substrates. Stationary mask openings over the targets and mechanical actuators that rotate the subtables in a precise manner were designed and incorporated to accomplish the linear and orthogonal stoichiometry variations. The effectiveness of the method was demonstrated for a $SiSn_xAl_y$ ($0 < x, y < 1$) film. Electron microprobe analysis showed the Sn content increasing parallel to one edge on the wafer and the Al content increasing in a perpendicular direction.

The advantages of this system are as follows:

(1) Intimate mixing of the elements (fast table rotation) or artificial layered structures (slow table rotation) are possible. This allows the production of amorphous phases. Libraries can be annealed after deposition to form stable thermodynamic phases, if desired.

(2) Composition variation is linear and orthogonal. Other compositional variations (e.g. parabolic, etc.) can be achieved by simply changing the profile of the mask openings.

(3) Large substrates can be used. For example, the method could be scaled to sputtering systems with 3 or 6 in. targets and a rotating substrate table to make 15 cm × 15 cm square films.

(4) The implementation of the system is simple and inexpensive.

(5) Patterned arrays of separate pixels can be produced by first placing a contact mask (laser cut from adhesive tape) directly on the substrate.

(6) Although our system is computer controlled, the $SiSn_xAl_y$ film described here could easily be made under manual operation, because once all targets are powered and the table is rotating, no adjustments need be made.

The construction of this system has allowed our research group to begin a program in combinatorial materials synthesis at modest expense, using an existing multitarget sputtering machine with a rotating substrate table.

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