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The "Multiple-Sample Concept" in Materials Research: Synthesis, Compositional Analysis and Testing of Entire Multicomponent Systems

J. J. HANAK
RCA Laboratories, Princeton, New Jersey, USA

This paper questions the efficiency of the present approach to the search for new materials which consists of studying only one composition at a time. A new concept of materials research is introduced which consists of synthesising, analysing, testing and evaluating of large parts of multicomponent systems in single steps. Implementation of this concept has been possible through the development of a one-cathode, multiple-target, radio-frequency co-sputtering method of synthesis and of a novel, simple method of compositional analysis of any co-sputtered film, based on film thickness measurements. An example is given of the use of such an approach in studying new binary superconducting compositions, which resulted in a thirty-fold increase in the rate of finding new materials. A several hundred-fold increase in research productivity is predicted for higher-component systems.

1. Introduction

The present approach to the search for new materials suffers from a chronic ailment, that of handling one sample at a time in the processes of synthesis, chemical analysis and testing of properties. It is an expensive and time-consuming approach, which prevents highly-trained personnel from taking full advantage of its talents and keeps the tempo of discovery of new materials at a low level. Significant increase in the productivity in materials research can be realised by abandoning this duplication of effort and adopting the concept of processing many different materials at the same time. In order to introduce this concept, the approach to synthesis must be changed so that a large part of a given multicomponent system is synthesised at one time; the approach to chemical analysis must be revised so that analysis for the entire system can be obtained by a computer method based on a few simple measurements; finally, efficient methods of materials testing and evaluation must be introduced which can characterise such a system in one experiment. These steps are summarised in fig. 1.

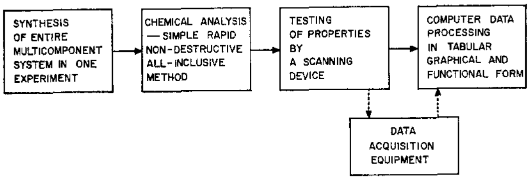

Figure 1 Flow chart of processes needed for the study of entire multicomponent systems in single steps.

The possibilities implied by this concept in the search for new materials are indeed intriguing; hence, steps have been taken toward implementing it. A brief review of pertinent status and advances in synthesis, chemical analysis and materials testing will be given first, any missing links will be pointed out and the solutions to remaining major obstacles will be described.

1.1. Recent Advances in Materials Synthesis

In recent years several groups of scientists took a significant step toward abandoning the traditional method of materials synthesis by using a technique of co-evaporating [1] or co-sputtering [2-7] of two or more elements from different, physically separated sources onto a suitable substrate. In this manner they were able to obtain, in one experiment, almost the entire composition continuum of a given binary or ternary system deposited on one substrate. Co-sputtering is preferable to co-evaporation because of the ease of deposition rate control. As it is desirable to co-sputter as large a combination of materials as possible, radio-frequency sputtering is preferable since it is capable of sputtering electrical conductors and insulators alike. One of the objectives of the present work, therefore, was to develop a simple, general, radio-frequency co-sputtering method applicable to co-deposition of nearly entire binary and ternary systems.

1.2. The Problem of Material Analysis

Specimens made by the foregoing techniques have to be analysed for chemical content point by point by existing chemical or physical methods. Thus the advantage gained by the synthesis technique was all but lost in the analytical methods.

Analytical methods which are attractive for use in conjunction with the synthesis techniques described above are the non-destructive physical methods, capable of scanning over large areas of composition as, for example X-ray fluorescence and electron-probe analysis. However, these methods require calibration standards for each new combination of elements. Normally, they are specific for certain classes of materials, i.e. they are not inclusive for all elements and all compositional ranges. In addition, rather complex instrumentation and highly trained personnel are needed to perform the analysis. All of these factors contribute to both the high cost and to long delays in performing chemical analysis.

For thin films containing entire multicomponent systems prepared by the techniques mentioned above, it would be highly desirable to develop a rapid, inexpensive, analytical technique applicable to all solid substances alike, which, in addition, would not require a new calibration for each combination of elements. Therefore, the second object of the present work was to develop such a technique, based on the measurement of some simple property such as film thickness.

1.3. Recent Advances in Materials Testing and Evaluation

In the category of testing and evaluation fall all conceivable chemical, physical and mechanical properties, each of which requires a different testing device. It is beyond the scope of this communication to attempt to summarise the existing "state of the art" of the methods for testing these properties. Suffice it to say, that many of them are capable of scanning large areas of a given specimen and hence are capable of determining simultaneously or sequentially the properties of the entire composition range in the specimen.

2. Implementation of the "Multiple-Sample Concept"

As the first step toward implementing the "multiple-sample concept", a radio-frequency co-sputtering technique has been adopted and simplified, which is capable of synthesising nearly complete binary and/or ternary solid alloy systems in one experiment, regardless of the constituents or their miscibility. Next, a unique computerised analytical method has been developed which is based on the measurement of a simple extensive property common to *all* deposited films, namely, the thickness. *In order to obtain analysis for the entire composition range the only required measurements are two thickness measurements for a given binary system or three such measurements for a ternary system.* The development of this method has meant the removal of the main obstacle to the realisation of this concept.

With these methods of synthesis and analysis it was possible to undertake the search for new materials in any of several classes of materials of interest to our research. The first class chosen was that of superconducting materials because of their common property, the transition temperature (T_c), which is extremely sensitive to compositional variation. The cryogenic testing was performed with a device capable of measuring the T_c of an entire binary system in one experiment. In five months of using this approach, many new superconducting materials have been found [5, 6]. The impact of this approach was noted primarily in the productivity, which increased thirty-fold over that of the traditional approach. Some of the technical details of these developments, primarily of the composition analysis, are given in the following technical discussion.

2.1. Synthesis of Multicomponent Systems by Radio-Frequency Co-Sputtering

The reason for choosing radio-frequency co-sputtering as the method of synthesis is that it is capable of depositing a greater variety of substances than any other technique and because any of these substances can be made to mix with others in all proportions in sputtered films. It is thereby possible to obtain not only ordinary compounds and solid solutions, but also metastable mixtures and compounds. By selecting the appropriate substrate and substrate temperature or annealing temperature it is possible to grow films with structures ranging from the amorphous state to microcrystalline polyphase mixtures, polycrystalline single phase, and also epitaxial single crystals.

The experimental details of the radio-frequency co-sputtering technique were the following. A diode radio-frequency sputtering module was used with a single disk-shaped target electrode, 15 cm in diameter, at the bottom and the substrate holder on top. This arrangement facilitated a simple positioning of various targets on the electrode without the need to fasten them. For the deposition of two-component films, the target and substrate arrangement shown in fig. 2 was used. The target consisted of two half disks of two different materials A and B placed on the radio-frequency cathode. The substrate consisted of a flat plate 12.7 cm long by 1.27 cm wide, made of glass, ceramic, or metal placed parallel to the surface of the target and perpendicular to the A-B interface. Material deposited in the form of a narrow strip thus varies continuously in composition along the length of the substrate. The range of composition is dependent on the relative sputtering rates of A and B; when these were nearly equal, approximately 70% of the range of compositions could be sputtered on one substrate.

For co-sputtering of three-component systems, the target and substrate arrangement shown in fig. 3 was used. The targets consist of 120° sectors of a disk of three different materials A, B and C. The substrate is in the form of a disk placed parallel to the composite target.

For both the binary and ternary systems other additional target subdivisions were used to compensate for widely varying sputtering rates. The inconvenience of requiring different target geometries can be circumvented by the use of separately powered electrodes [3, 7, 8], however, this requires well-controlled radio-frequency and/or DC power into each of the electrodes. The use of one electrode for several targets eliminates the need for close power control since the sputtering rates of all components vary in the same proportions as power fluctuations.

The reason for using a strip substrate for binary systems and a disk substrate for ternary is based on an easily-deduced generalisation which states that the dimension order N of a substrate for depositing an n-component system is

$$N = n - 1 \tag{1}$$

The same relationship applies to the arrangement of the targets, although this can be best visualised when the targets are reduced to point sources. Equation 1 implies that it is impractical to deposit an entire continuum of compositions for more than a three-component system. A four-

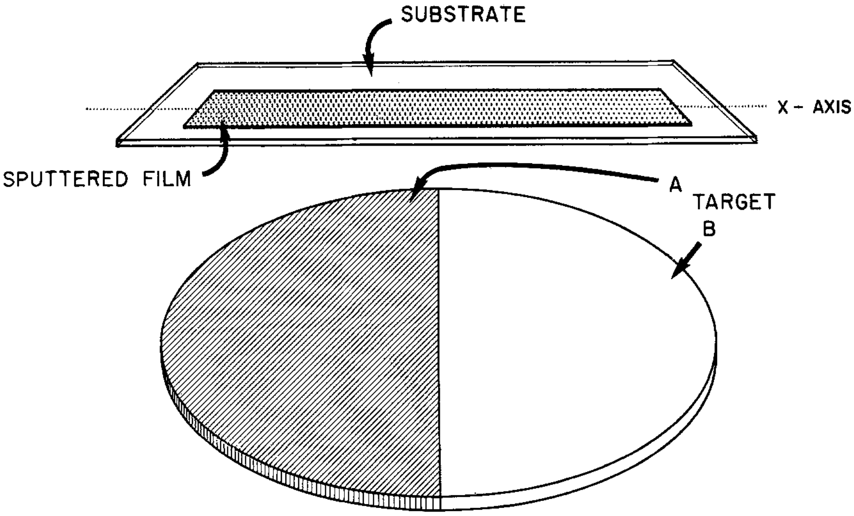

Figure 2 Schematic arrangement for co-sputtering of two-component systems.

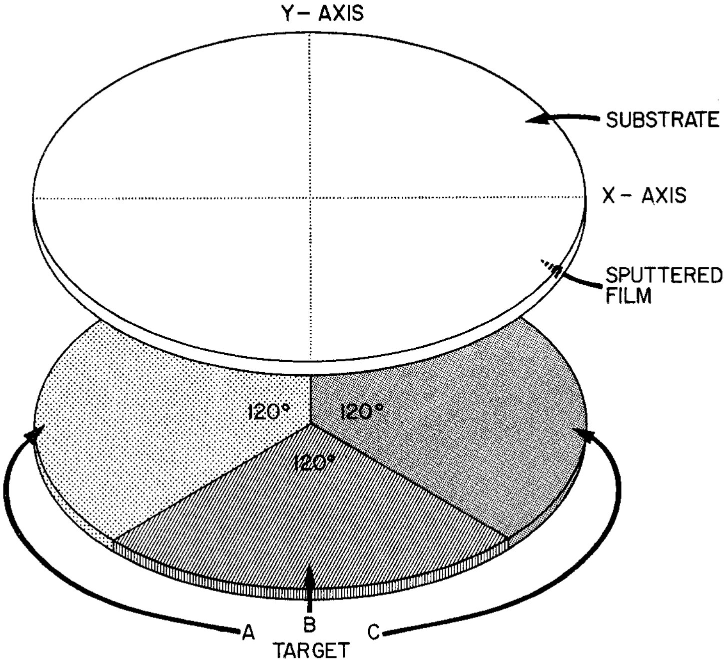

Figure 3 Schematic arrangement for co-sputtering of three-component systems.

component system, for instance, would require a hollow, three-dimensional substrate. Concentric arrangement of target rings [4] can be useful for deposition of binary systems on one substrate, however, not for entire ternary or higher systems.

Sputtering experiments were carried out at a radio frequency of about 10 MHz, constant argon pressure of 10 μm and constant target to substrate distance of about 5 cm. Radio-frequency power setting was adjusted to suit a particular experiment. As the targets were not in a good thermal contact with the water-cooled electrode at higher power settings, considerable heating of the targets took place and in certain instances, in particular in the case of lower melting metals such as Al, Sn, Mg and Au, serious cross-contamination of the surface of the targets took place. This was evident from the darkening of the target and the lowering of the sputtering rates from that target. High melting metal targets such as Mo and Nb sputtered in combination with the preceding metals were not visibly contaminated. The cross-contamination problem has been essentially eliminated by using lower power at which the targets remained cool.

The major uncertainty of sputtering from a composite target placed on one electrode was whether two electrically dissimilar substances (e.g. metal and a dielectric) would co-sputter at all and, furthermore, whether with relative rates similar to those of full disk targets. By means of composition analysis (to be described below), it has been shown on several co-sputtered materials, including metal-metal pairs and metal-dielectric pairs, that at a given radio-frequency power the sputtering rates per unit target area remained within $\pm 25\%$ for partial and full disk targets of a given material. This variation is not critical as long as the sputtering rates are finite and remain constant in a given experiment.

2.2. Novel Compositional Analysis of Radio-Frequency Sputtered Films

The advantage of the preceding method of synthesis is that the same method can be used for practically any chosen multicomponent system. The same would be desired of an analytical method; however, in addition, it should be inexpensive, non-destructive and applicable to thin films. There is no such previously established method in existence. In the course of this work such a method has been developed by recognising that it is possible to calibrate a sputtering apparatus and that a simple extensive variable, the film thickness, contains enough information to carry out the analysis.

Let us consider the deposition of a narrow film strip from a sputtering geometry shown in fig. 2. After the deposition the amounts of each of the components in the film at any point x along the length of the substrate are designated by $T_A(x)$ and $T_B(x)$. Each of these quantities can be expressed as a product of a number of constants and of another variable, as for instance,

$$T_A(x) = tR_A(O)G_A(x)\ . \qquad (2)$$

We may chose to name the constants t and $R_A(O)$ as the sputtering time and the sputtering rate, respectively, at some arbitrarily defined point and the variable $G_A(x)$ as the deposition profile. We may interpret $T_A(x)$ as the hypothetical film thickness of component A. Assuming superposition (i.e. Vegard's Law), the total film thickness $T_{AB}(x)$ at any point x is equal to the sum of individual thicknesses, $T_A(x) + T_B(x)$, which, from equation 2 is equal to

$$T_{AB}(x) = t[G_A(x)R_A(O) + G_B(x)R_B(O)]\ . \qquad (3)$$

Equation 3 is the key to the chemical analysis of the deposited film. It states that the total thickness at any point x can be represented as the sum of the products of known time, the deposition profiles (which can be determined beforehand as will be shown presently) and of unknown rates $R_A(O)$ and $R_B(O)$. As implied in equation 2, these rates remain the same for the thicknesses at any point. Thus, the solution for $R_A(O)$ and $R_B(O)$ can be obtained from a pair of thickness measurements made at any two different points on the substrate.

Once the values of the two rates have been calculated, one can solve for $T_A(x)$ and $T_B(x)$ at any point by means of equation 2, for total thickness by means of equation 3 and for composition in terms of volume % by means of equation 4:

$$\text{vol}\ \%\ \text{A} = \frac{T_A(x)}{T_A(x) + T_B(x)} \times 100\ \cdot \qquad (4)$$

Composition in terms of mole % can be obtained with the knowledge of density and atomic weight of each of the components.

The magnitude of error can be estimated from the following equation, when one assumes Vegard's Law and the absence of compensating errors,

$$\%\ \text{error in A} = \frac{T_{AB}(x)_{\text{measured}} - T_{AB}(x)_{\text{calculated}}}{T_{AB}(x)_{\text{measured}}} \times 100\ \cdot \qquad (5)$$

Derivation of similar analytical procedure for any number of components deposited on a planar substrate (fig. 3) and having target sectors of equal or unequal areas proceeds in a similar manner. For the general case of n sector targets, the expressions for individual thicknesses $T_J(x, y)$ are similar to equation 2 and the expression for the total thickness $T_{AB\ldots n}(x, y)$ is similar to equation 3, namely,

$$T_{AB\ldots n}(x, y) = t[G_A(x, y)R_A(O, O) + G_B(O, O) + \ldots + G_n(x, y)R_n(O, O)]\ . \qquad (6)$$

In each multicomponent system the minimum number of thickness measurements needed is equal to the number of different targets. Since thickness measurements are very easy to perform, it is desirable to make use of them in order to obtain greater accuracy in determining the rates $R_J(O, O)$ and thereby greater accuracy in the determination of composition.

Regarding the deposition profile, it is important to point out that its definition is arbitrary until specified; only the product $G_A(x)R_A(O)$ in equation 2 remains invariant. The definition of the deposition profile adopted in this work for deposition onto a planar x,y substrate such as in fig. 3 from any target sector is

$$G_J(x,y) = \frac{\theta}{2\pi}\frac{W_J(x,y)}{W_J(O,O)} \qquad (7)$$

where θ (in radians) is the angle between the radii of the sector; $\theta/2\pi$, the ratio of the areas of the target sector and of a full target disk; $W_J(x,y)$, the amount of component J at any point x,y on the substrate; and $W_J(O,O)$ the amount of component J at the origin. Once the definition of the $G_J(x,y)$ has been specified, so has the significance of the rate $R_J(O,O)$. Thus, with the definition used in equation 7, $R_A(O)$ and $R_B(O)$ in equations 2 and 3 or $R_A(O,O)$, $R_B(O,O)$ in equation 6, becomes the deposition rate at $X = 0$ for full disk targets of A or B.

The determination of the deposition profiles can be performed by first depositing a film of two or more components from sputtering geometries, such as shown in figs. 2 and 3, then by performing a chemical analysis of the amounts $W_J(x,y)$ of each of the components at a sufficient number of points and, finally, by the use of equation 7, calculating the profiles. Since $G_J(x,y)$ in equation 7 is a normalised quantity, $W_J(x,y)$ need not be in absolute units. Some convenient relative units varying directly and linearly with the absolute amounts will suffice, as for instance, X-ray fluorescence intensity data. The results of such a determination for two half-disks are shown in figs. 4a and b. X-ray fluorescence intensity data for molybdenum-niobium alloys have been used to obtain the profiles.

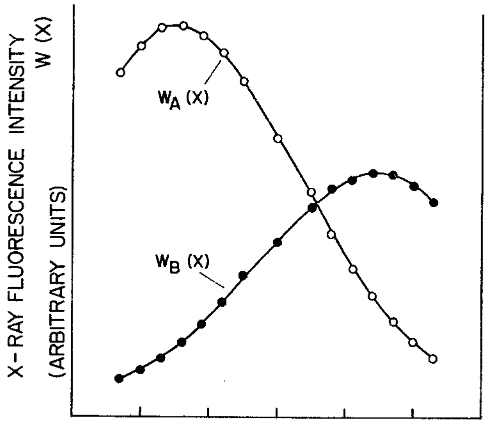

Figure 4a X-ray fluorescence intensity data as a function of substrate position for Mo–Nb alloys co-sputtered from two half-disk targets (A = Mo, B = Nb).

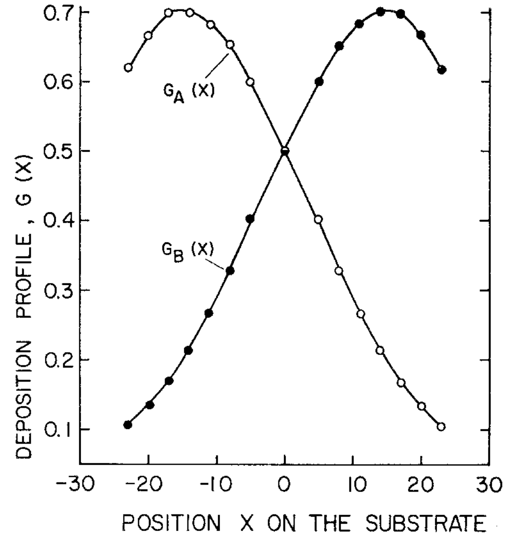

Figure 4b Deposition profiles for two half-disk targets as a function of substrate position.

It would be desirable to make use of theoretical expressions for the deposition profiles; however, they are available only for targets having simple geometries such as disks [9, 10] or rings [4]. Work is currently in progress toward the use of existing theoretical profiles in the preceding analytical procedure and toward the development of theoretical profiles for more complicated geometries.

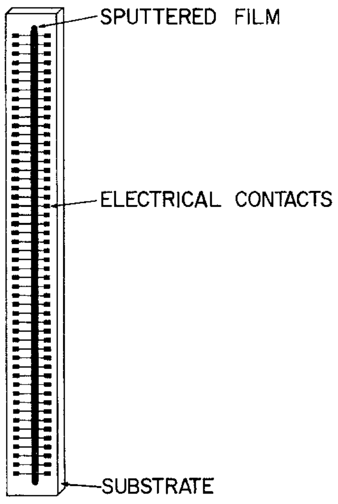

Figure 5 Substrate for the deposition of binary superconducting materials.

An example of the use of this analytical technique is given for Ag-Al_2O_3 cermets, co-sputtered from the two half-disks of silver and alumina onto a glass substrate as shown in fig. 5. The thickness of the film was measured along the entire 12.5 cm long substrate by the Tolansky method at 0.25 cm intervals. A least squares fit was made of ten such thickness points $T_{AB}(x)$ (five from near each end of the substrate in fig. 5) and the corresponding deposition profiles $G_A(x)$ and $G_B(x)$ (fig. 4) in equation 3 in order to obtain the deposition rates $R_A(O)$ and $R_B(O)$. The resulting rates were then used in computing the hypothetical thicknesses $T_A(x)$ and $T_B(x)$ of the individual components from equation 2, the total thickness $T_{AB}(x)$ from equation 3 and the composition in volume % from equation 4, all at any desired position x on the substrate. The observed and calculated total thicknesses appear in fig. 6 along with the analytical results. Most of the deviations in thickness were random and within the experimental error of the thickness measurements. The excellent agreement of the thickness results is taken as a positive test of this analytical method. Extensive use of the two-component sputtering on known and new superconducting materials has shown that the known compounds occur at calculated compositions which are within ±5% of the composition of such compounds.

The compositional analysis technique just described can also be used, without actual sputtering of the alloy film to *predict* its composition and thickness as a function of position from known deposition rates from *full disks*,

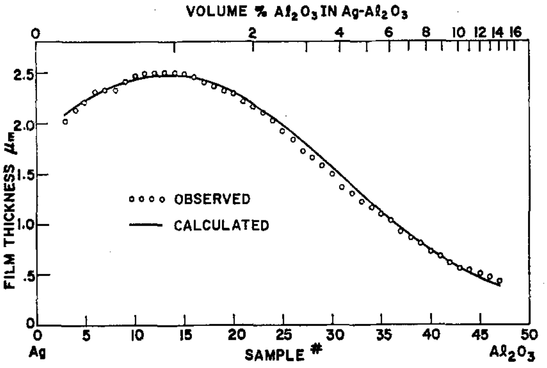

Figure 6 Calculated composition and calculated and observed thickness of co-sputtered Ag–Al_2O_3 cermet mixtures as a function of substrate position.

$R_J(O)$, and from known deposition profiles. This is done by first determining the sputtering rates for full disks of each component above the centre, or by using the values of sputtering rates calculated from other co-sputtering experiments and then by the application of equations 2 to 4, calculating the predicted thicknesses and compositions. This is a useful procedure for deciding which target geometry should be used in order to obtain a desired composition, or where to place a small substrate on which such composition is to be deposited.

2.3. Application of the "Multiple-Sample Concept" to Superconducting Materials Research

The "multiple-sample concept" has already been introduced and successfully tested in the search for new superconductive materials in binary systems. Alloys with continuous ranges of composition were deposited in the form of a strip onto a substrate shown in fig. 5. Fifty gold contacts were evaporated along the alloy strip so that superconducting transition temperature (T_c) and resistivity could be measured at regular composition intervals of about 2%. A cryogenic testing device, capable of rapid testing of all the composition intervals in one experiment, was used. The raw test data were then processed and plotted automatically by means of a computer, as shown in fig. 7, which shows superconducting transition temperature and the resistivity of co-sputtered Mg-Mo mixtures [6].

The five months' operation of this novel approach has furnished useful data for making a realistic comparison between it and the traditional approach. The present rate of output of experimental results is about thirty times that of the old approach. This ratio applies to the binary systems; for ternary systems the number of compositions, at 2% intervals, is higher by a factor of 25, yet the time spent for characterising such a system by means of the "multiple-sample concept" is expected to be essentially the same. *Hence, the expected ratio of increase of information output and overhead decrease is 750 to 1 for ternary systems.* The same ratio would apply to quarternary systems, since it is physically impractical to synthesise the complete system in one run, but in step increments of the fourth component.

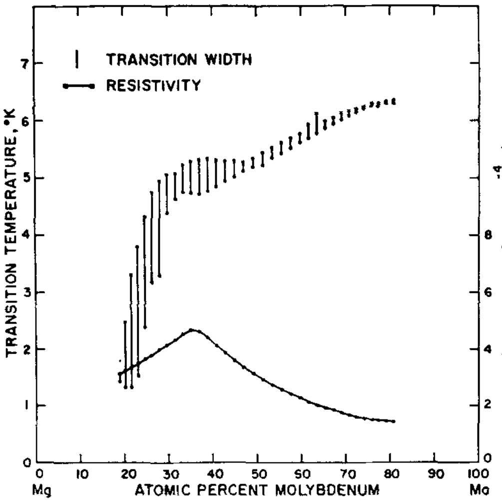

Figure 7 Superconducting transition temperature and electrical resistivity of co-sputtered Mo–Mg films.

This approach to materials research can be applied to other classes of materials as well. Its main use can be as an exploratory tool for scanning a large number of materials for desired properties and then for optimisation of existing materials, such as doping or alloying of known materials to improve their performance. When new materials are found or the existing materials are optimised, other methods of synthesis may be employed to synthesise such materials if sputtering is impractical. On the other hand, this approach can be looked on as the actual fabrication technique for many materials whenever they are used in a film form.

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