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APPLICATIONS OF THERMOANALYTICAL METHODS TO THE STUDY OF THIN FILMS

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Studies of the formation and properties of thin films is a growing area in both science and technology. Characterization of these films and the processes by which they are prepared is a major factor in understanding, controlling, and optimizing their synthesis and usefulness.

Thermal methods can play an important role in such studies, provided that they can overcome the difficulties imposed by the massive amount of associated substrate. Unless one is studying the film - substrate interaction, the substrate's presence only serves to decrease the sensitivity by diluting or reducing the thermal effect being measured.

The three basic strategies that have evolved are discussed and examples described. One approach is to remove the film from the substrate, when this is appropriate and feasible, and then study the film separately. A second method is to use larger samples and careful measurements in an effort to overcome the reduced sensitivity. The final means is to develop very sensitive and/or selective techniques to investigate the film and its potential interactions with the substrate.

Keywords: application of TA, thin films

Introduction

Thin films are playing an increasing role in many aspects of modern technology. The ability to characterize them adequately is vital to being able to provide the necessary feedback from the film's properties to the synthesis procedure. This loop is necessary in order to optimize overall process. One of the major tools used in the characterization of materials is thermal analysis. There are some disadvantages, however, imposed by working with thin films.

The main problem is associated with the decline in the sensitivity of the methods due to the enormous dilution effect as a result of the massive substrate. The weight and heat capacity of the substrate overwhelms the small contribution due to the material of interest, the thin film. Consequently, great

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sensitivity is required and one is frequently faced with measurements involving the difference between large numbers.

Sawada and Mizutani [1] have reviewed much of the early literature on the topic and described many studies of films that have been separated from the substrate prior to thermal analysis. Under these conditions, of course, the thermal analysis is essentially unchanged from the traditional mode. They also describe the usefulness of thermal analysis to study the important properties of the raw materials used in the preparation of the films.

This paper will concentrate the author's experiences working predominantly in the area of electronic materials. It will be divided into two sections. The first will deal briefly with separated films. The second will be concerned with films still on their substrates. The latter topic will be subdivided into a section which deals with applying conventional thermal analysis and one concerned with methods to enhance the sensitivity.

Separated films

Parylene is a relatively stable polymer for use as a dielectric material the fabrication of semiconductor chips. Its thermal stability is a limiting factor in its potential use. This stability depends strongly on the oxidizing power of the ambient. Figure 1 shows TG curves for parylene films that have been stripped from silicon wafers and heated at 10 deg·min^{-1} at atmospheric pressure in various concentrations of oxygen. The onset of weight loss varies consider-

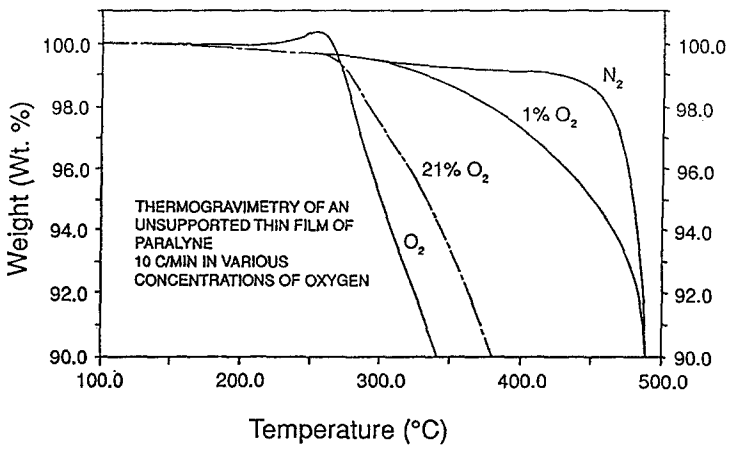

Fig. 1 TG curves at 10 deg·min^{-1} for the degradation of Parylene in different concentrations of oxygen

ably and clearly indicates that any higher temperature processing steps subsequent to the films deposition should be conducted in an inert atmosphere. There is also a small amount of oxygen uptake evident for the material in pure oxygen prior to the decomposition.

Iron oxide films have been successfully used as masks for the optical exposure of photoresist materials [2]. These films are prepared by the chemical vapor deposition (CVD), reacting iron carbonyl with oxygen on the surface of the fused quartz substrate. Exposure of the film to a laser or electron beam converts the exposed area to a less soluble form. After a subsequent treatment the desired opaque pattern remains. The chemistry of this exposure process is related to the stability and nature of the deposited film.

Thermoanalytical techniques were used to study the nature of the conversion from readily soluble to relatively insoluble material for both a CVD film and one prepared by conventional reactive sputtering techniques [3]. The film was removed from the substrate by scraping with a blade. Flakes of both films were examined by TG and DTA in air at 20 $deg \cdot min^{-1}$. The CVD film showed a weight loss of about 10 wt% around 300°C while the sputtered film lost only 1 wt%. The CVD film also exhibited a clear exotherm at this temperature and the sputtered film showed no features. IR and Mössbauer spectra indicated that the CVD film had a large fraction of the iron present in the divalent state as well as a considerable carbonate concentration. The ease of solubility of the unexposed CVD film was thereby readily explained. The laser or E-beam exposure converts the partially decomposed material completely to the relatively insoluble α-Fe_2O_3.

Supported films

Conventional methods

It is possible to perform TG under sufficiently careful conditions that the extra weight of the substrate does not prove prohibitive. A thin film of carbon is used as a coating on optical fibers to reduce the exposure to water and the concomitant formation of hydroxyl groups in the fused silica. Such hydroxyl linkages attenuate the optical signal. The film is produced at high temperature during the fiber pulling process. Figure 2 shows that it is possible to measure the combustion of this carbon and, hence, its amount. An assumption of the fiber's geometry and the film's density will allow calculation of the film's thickness.

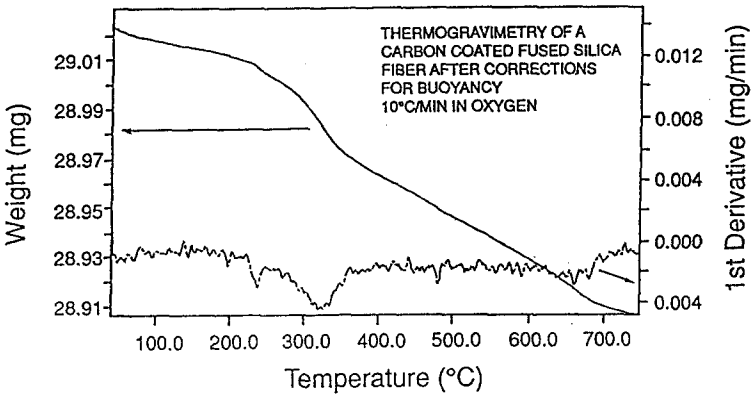

Fig. 2 TG and DTG curves after corrections, for a carbon coated fused silica fiber at 10 deg·min^{-1} in oxygen

Buoyancy and aerodynamic corrections are comparable to the weight change under investigation and therefore the compensation becomes critical for accurate work. Fortunately the substrate remains unaffected so that it is possible to reheat the same sample under identical conditions and subtract this reheat as a baseline correction. The TG and DTG curves in Fig. 2 are after this corrective process. They indicate how well a weight change of only 100 μg can be monitored for a sample size of 30 mg.

Superconducting niobium nitride films were of interest for potential use in Josepheson junction devices. The necessary thin insulating film is made by controlled oxidation of the nitride surface. Films were sputtered onto thin substrates and careful TG experiments were able to follow the kinetics of the oxidation process for films as thin as 0.32 μm [4]. The apparent activation energy of 44 kcal· mol^{-1} was in excellent agreement with the value derived earlier [5] of 45–50 kcal· mol^{-1} for bulk powders.

Many films as they are deposited form in an amorphous or microcrystalline fashion, particularly if the substrates are unheated. Either DTA or DSC can be used to detect the exothermic transformation from the metastable unordered state to the stable crystalline form. Examples of this are IrO_2 [6] and $TaSi_2$ [7] films. The sensitivity can be markedly enhanced by placing the film side in contact with the sensor rather than film side up.

More sensitive techniques

Cobalt films have been successfully studied using thermomagnetometry (TM) [8]. The small weight change that would be associated with the oxidation of a 75 nm film of Co is obviously very small, however it can be made to appear much greater by utilizing the strong magnetic attraction of the metal. Figure 3 shows both the oxidation and subsequent reduction of the film on a sapphire substrate. The weight in the absence of a magnetic field gradient is 33.05 mg. When a reasonably small field gradient of about 300 Oe cm^{-1} is imposed on the sample it gains apparent weight to 33.8 mg.

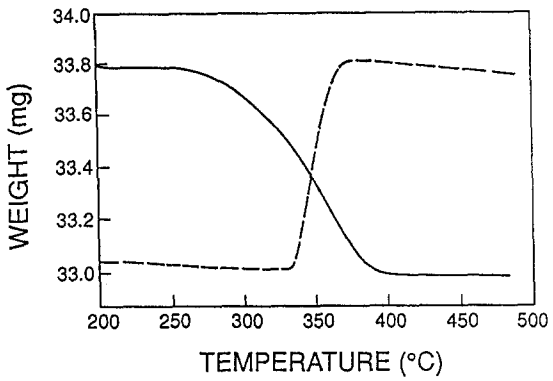

Fig. 3 TM curves for a 75 nm film of Co on sapphire. The solid curve represents the original heating in O_2 and the dashed curve is for the oxidized film reheated in 15% H_2 in N_2

As the film is heated at 1 deg·min^{-1} in oxygen cobalt oxides are formed and the ferromagnetic metal is consumed. With no ferromagnetic material remaining the weight is essentially what it would be in the absence of the field gradient. After the sample is cooled and reheated in 15% H_2 in N_2, it follows the dashed curve. The weight gain represents the reduction of the oxide and formation of the metal. The sample returns to very near its original weight in the field. The apparent weight changes are sufficiently large that kinetics may be easily followed. It must be kept in mind, however, that the measurement is not following the rate of formation of the oxide but rather the consumption of the metal.

Similar studies were conducted between the pole faces of a strong electromagnet. The sensitivity in a stronger field is such that one can nearly follow the oxidation of a monolayer. When a cobalt film was placed on a silicon substrate it was even possible to follow the formation of cobalt silicide by this technique. This reaction involves no intrinsic weight loss, only the apparent weight change associated with the magnetic attraction. Clearly, if one

of the reactants or products is strongly magnetic, this can be exploited to enhance the sensitivity of the measurement.

The great sensitivity of a mass spectrometer can be utilized to study the evolution of very small quantities of volatile species. This EGA method is more sensitive when the sample is decomposed directly in the vacuum system in close proximity to the ionizing elements of the instrument [9, 10]. This type of instrument also allows determination of readily condensible species which would not pass through even a heated leak. The disadvantage is, of course, that one can not control the atmosphere and must extrapolate the observation back to atmospheric pressure for comparison with conventional TG, DTA, or DSC results.

A naturally occurring thin film results from corrosion. In a recent study on copper corrosion conducted in conjuction with the refurbishing of the Statue of Liberty in New York harbor, an MS-EGA study of corrosion products on copper was performed [11]. As can be seen in Fig. 4 there are a great many products formed on the surface by the natural corrosion in an urban and oceanside environment. Comparison of EGA and X-ray diffraction data with known minerals provided a description of the corrosion film.

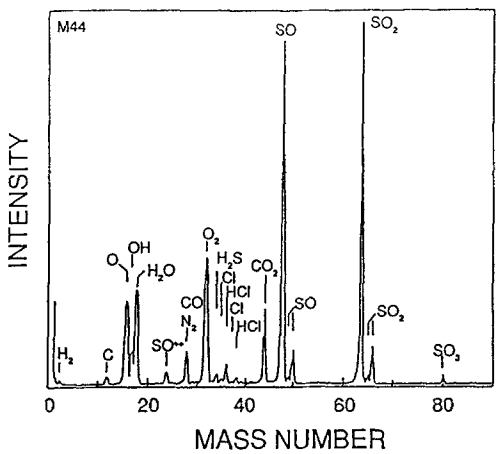

Fig. 4 MS-EGA Curve at 530°C for the thermal decomposition of a corrosion film on copper

In processing of GaAs semiconductor devices, it was frequently noted that the electrical contacts failed. These contacts were made by evaporating thin films of gold in a prescribed pattern on the semiconductor surface. Examination by MS-EGA showed that the loss of ohmic contact was due to the reaction of the underlying semiconductor substrate with the conducting pad [12].

Figure 5 shows that arsenic vapor was released at a much lower temperature than was predicted based on known decomposition temperature of GaAs. The amount of arsenic released scaled directly with the amount of gold present. The degradation involved the dissolution of gallium into the gold and the release of the freed arsenic.

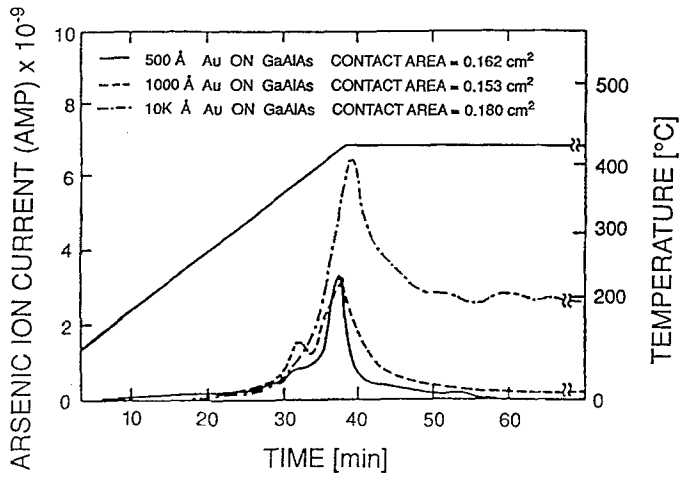

Fig. 5 MS-EGA curve for the evolution of As from GaAs in contact with Au films

Two final examples are presented to demonstrate the importance of MS-EGA in VLSI processing. Films of boron nitride are used for masks in X-ray lithography. The critical flatness of these masks is frequently destroyed by stresses in the film which cause a bowing of the film and substrate. These films are formed by a CVD process involving diborane and ammonia. The incorporation of significant amounts of hydrogen into the films was revealed by MS-EGA. Figure 6 shows a typical curve for the evolution of hydrogen [13]. There are several bonding sites for the hydrogen which were characterized by NMR and IR spectroscopy. The EGA was used to show how the more weakly held hydrogen around 500°C was responsible for the stresses and what annealing conditions were required to alleviate the problem.

One of the more interesting studies concerned the loss of adhesion by conducting films of tantalum silicide on silicon [7]. This process occurred when the devices were heated to about 1000°C to flow the protective dielectric layer of a boro-phosphosilicate glass. During this process blisters formed in the softened glass suggesting that the evolution of a gas may be the cause of the problem. As can be clearly seen in Fig. 7, there is an evolution of significant quantities of Ar at that temperature. There is also a smaller evolution

near 300°C where the DSC curves showed an amorphous to crystalline transition. A program was instigated to utilize EGA to optimize the sputtering conditions to minimize the incorporation of argon into the tantalum silicide films.

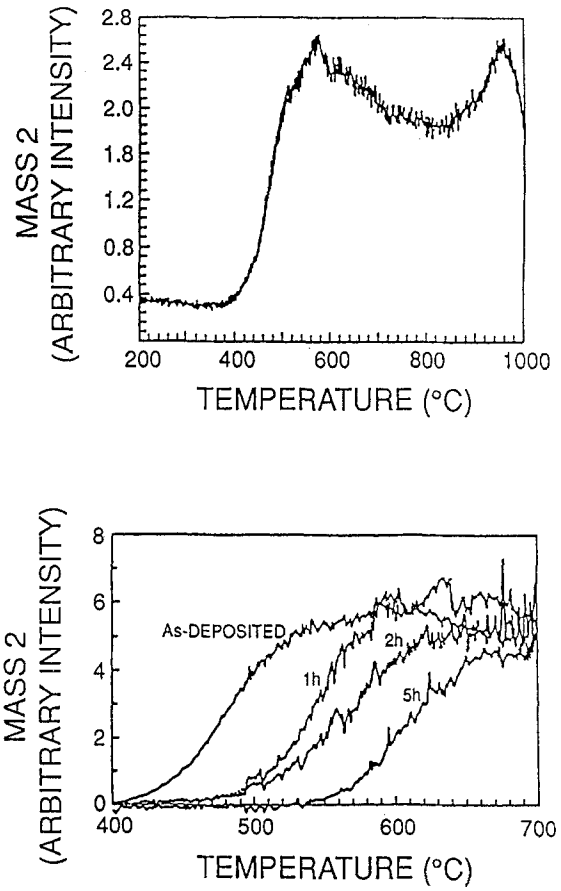

Fig. 6 MS-EGA curve for H_2 in BN films

Emanation Thermal Analysis (ETA) is another sensitive method that has been used to characterize thin films prepared by sol-gel or CVD methods. ETA is based on the release of radioactive inert gas atoms from a solid sample as the temperature is increased. The solid has been previously implanted with the gases or a radioactive parent such as ^{228}Th or ^{224}Ra was incorporated into the solid during its synthesis [14]. The evolution of gas can be correlated with transitions, decompositions and densification of the film.

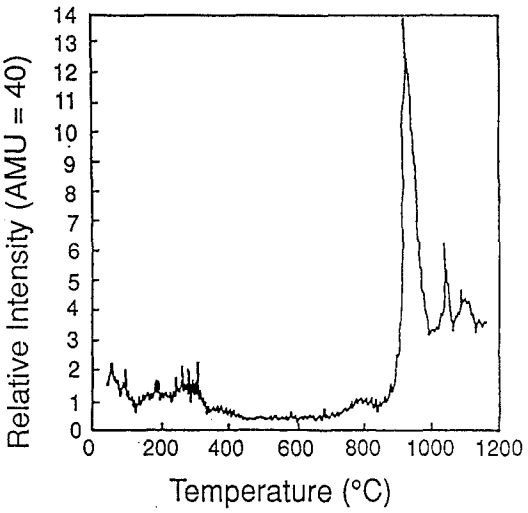

Fig. 7 MS-EGA curve for Ar in $TaSi_2$ films

The method has been used to follow changes int the porosity of titania films prepared by sol-gel techniques on glass substrates [15]. Similarly films of ZnS, prepared by CVD techniques using various precursors, were studied [16]. Recommendations for the optimization of the film's properties and processing were made based on the results of ETA.

Conclusions

Although it is more difficult to work with thin films, thermal analysis can play an important role in the characterization of these materials. Films can be detached from the substrate and run in a conventional manner. This precludes studying the film–substrate interaction, however. The properties of the film may also be changed by the process used to separate the film.

Consequently, it is often necessary or advisable to study the supported film. More attention must be given to the thermoanalytical technique in order to obtain meaningful data under these circumstances where the mass and heat capacity of the substrate dominate. Enhancement of the sensitivity for TG can be achieved if one of the reactants or products is magnetic. Use of TM can be sensitive to almost the monolayer level from strongly magnetic materials.

A very high degree of sensitivity can be obtained using MS-EGA techniques, particularly when the sample is contained within the vacuum system. This method can detect, not only the conventional gases such as CO_2, H_2O,

H_2, etc., but also can measure condensible species such as As, Zn, Li, etc. This enhanced sensitivity is particularly useful in studying the processing effects in semiconductor fabrication.

Another sensitive method is ETA. It is particularly applicable for studying changes in the nanostructure of films and powders.

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Zusammenfassung — Sowohl in Wissenschaft als auch in Technologie gewinnt die Untersuchung von Bildung und Eigenschaften dünner Schichten immer mehr an Bedeutung. Die Beschreibung dieser Schichten und ihres Herstellungsverfahrens ist ein wichtiger Gesichtspunkt zum Verständnis, zur Kontrolle und Optimierung ihrer Herstellung und Nutzbarkeit.

In derartigen Untersuchungen können thermische Methoden eine wichtige Rolle spielen, vorausgesetzt es gelingt diejenigen Schwierigkeiten zu überwinden, die durch die beträchtliche Menge assoziierten Substrates verursacht werden. Untersucht man nicht gerade die Wechselwirkung Schicht-Substrat, dann verursacht die Gegenwart des Substrates durch Abschwächung oder Verringerung des gemessenen thermischen Effektes lediglich eine geringere Empfindlichkeit.

Es werden die drei bestehenden Grundstrategien diskutiert und Beispiele beschrieben. Eine Lösung ist es, die Schicht, wenn es geeignet erscheint und möglich ist, vom Substrat zu entfernen und dann gesondert zu untersuchen. Eine zweite Methode ist die Verwendung größerer Proben und sorgfältiger Messungen, um die verringerte Empfindlichkeit zu überwinden. Die letzte Möglichkeit besteht in der Entwicklung empfindlicher und/oder selektiver Verfahren, um die Schicht und ihre potentiellen Wechselwirkungen mit dem Substrat zu untersuchen.