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THE USE OF THERMOMAGNETOMETRY TO FOLLOW REACTIONS OF THIN FILMS *

P.K. GALLAGHER, E.M. GYORGY, F. SCHREY and F. HELLMAN

AT & T Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)

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ABSTRACT

Thermomagnetometry (TM) is a useful technique to follow the appearance or disappearance of a magnetic phase. Even at relatively low magnetic field gradients, much greater sensitivity can be obtained with TM than with conventional thermogravimetry. This is demonstrated with a small permanent magnet by following the oxidation and subsequent reduction of cobalt thin films on sapphire and silicon using dynamic heating. Similarly, the reaction of cobalt and silicon is followed with this technique in an inert or reducing atmosphere. Isothermal oxidation at saturating magnetic fields provides a better defined and more sensitive experimental method to study the oxidation of cobalt.

INTRODUCTION

Most thermogravimetric (TG) studies of thin films are hindered by the large weight of inert substrate which requires compensation [1]. Note only does it dilute the percentage weight change which accompanies the process being monitored but also the corrections necessary for buoyancy and aerodynamic forces as a function of temperature are greatly increased by the large volume of substrate. In addition, there may be reactions of interest between the film and the substrate which would not generate a change in weight at all, e.g. a metal film on silicon which reacts to form a metal silicide.

However, if the film is ferromagnetic or ferrimagnetic in the temperature region of interest, it is then possible, by imposing a magnetic field gradient upon the sample, to markedly enhance the apparent weight change that may be associated with reaction, or for the case of metal silicide formation with a silicon substrate, to generate a substantial apparent weight change when none would otherwise occur. This technique known as thermomagnetometry (TM) has been used occasionally to study the formation of magnetic phases

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* We are particularly pleased to express our sincere appreciation to Professor Wendlandt for his many contributions to the thermoanalytical community. It is my (PKG) privilege to have served as Editor for this issue in honor of his 60th birthday.

and Curie temperatures in bulk materials, but rarely to study thin films [2]. It will be shown that the magnetic field gradient achieved through the use of a small permanent magnet is frequently all that is required to obtain a satisfactory measurement. Higher field strengths do, however, provide two advantages. Firstly, the uncertainty introduced into the analysis by samples which are not magnetically saturated is avoided. Secondly, the greater sensitivity allows the use of thinner films. Consequently, an example is also given of TM performed at a field sufficient to induce saturation in the cobalt film.

The oxidation of cobalt films on polished sapphire and partially oxidized silicon is used as an example of the method. The reduction of the oxidized cobalt film back to the metal is also shown. Finally, the reaction of a cobalt film with partially oxidized silicon to form a silicide is demonstrated. It must be kept in mind that the rate of formation of a specific product is not monitored, but rather the disappearance or appearance of one of the reactants, i.e. cobalt, is measured.

EXPERIMENTAL PROCEDURES AND RESULTS

Sputtered films of cobalt metal were prepared on polished sapphire plates. A film 750 Å thick was deposited on one plate and films 2100 Å thick were deposited on each side of a second plate. A film of cobalt 900 Å thick was deposited on a silicon water by chemical vapor deposition (CVD) from a cobalt carbonyl atmosphere. The silicon surface was lightly oxidized prior to deposition so that there was a SiO_2 barrier to a direct reaction forming the silicide [3].

A Perkin–Elmer Thermal Analysis System 7 was used for the TM studies

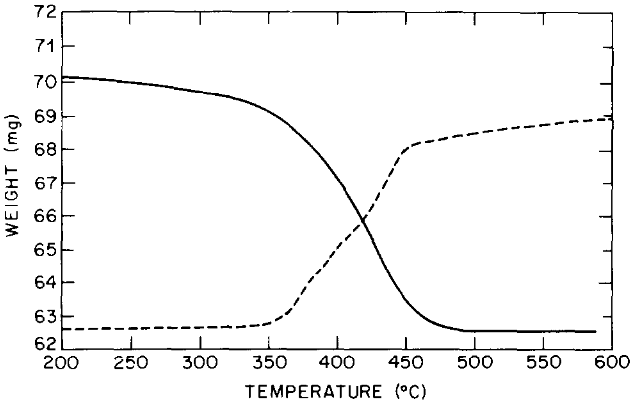

Fig. 1. TM curves for a cobalt film 2×2100 Å thick on single-crystal sapphire (about 30 mm^2) heated at 2° C min^{-1}: ———, in oxygen; — — —, subsequent reduction in 15% hydrogen and 85% nitrogen.

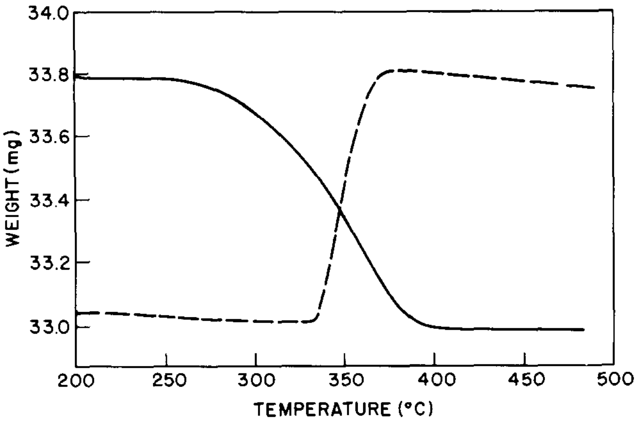

Fig. 2. TM curves for a cobalt film 750 Å thick on single-crystal sapphire (about 16 mm^2) heated at 1° min^{-1}: ———, in oxygen; — — —, subsequent reduction in 15% hydrogen and 85% nitrogen.

at low magnetic field strengths. Two small CoSm$_5$ permanent magnets produce 850 Oe and were used to provide the magnetic field gradient of about 300 Oe cm^{-1}. The film was placed in a horizontal position with the substrate side down resting on the platinum sample pan. An atmosphere of oxygen or forming gas (15% hydrogen in nitrogen) flowed at 60 ml min^{-1} down the tube over the sample. The magnet position was then adjusted to give the maximum apparent weight prior to heating.

Results for the oxidation of cobalt on sapphire are shown in Figs. 1 and 2 for the films of thickness 2–2100 Å and 750 Å respectively. A heating rate of 2° C min^{-1} was used for the 2–2100 Å film and 1° C min^{-1} for the 750 Å film. Figure 3 shows analogous results at 2° C min^{-1} in oxygen for the film about 900 Å thick on lightly oxidized silicon. The rates and temperature of

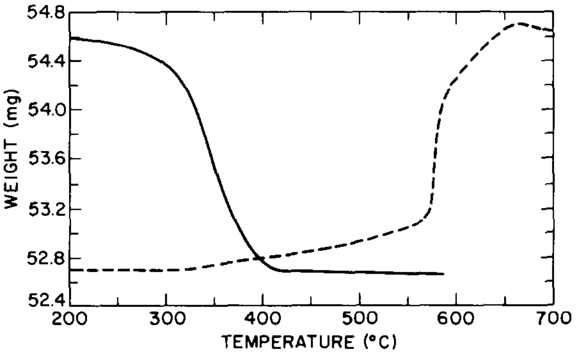

Fig. 3. TM curves for a cobalt film 900 Å thick on lightly oxidized single-crystal silicon (about 40 mm^2) heated at 2° C min^{-1}: ———, in oxygen; — — —, subsequent reduction in 15% hydrogen and 85% nitrogen.

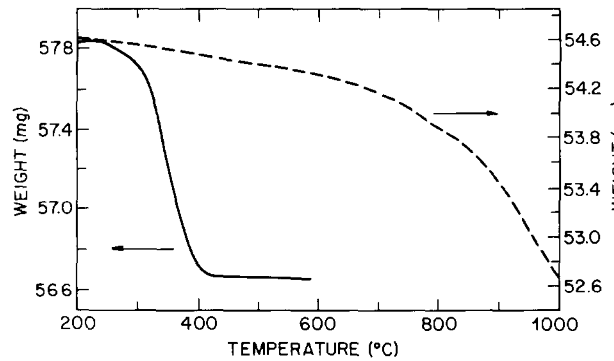

Fig. 4. TM curves for a cobalt film 900 Å thick on lightly oxidized single-crystal silicon (about 40 mm^2) heated at 2 °C min^{-1}: ———, in oxygen (oxide formation); — — —, in 15% hydrogen and 85% nitrogen (silicide formation).

the oxidation and reaction with the oxidized silicon are contrasted in Fig. 4 where the TM curves are shown for heating in oxygen and forming gas. The latter experiment results in the ultimate formation of silicide rather than oxide.

Typical scanning electron microscopy (SEM) micrographs of the as-deposited, oxidized and reduced films are shown in Figs. 5 and 6 for the cobalt films on sapphire and on lightly oxidized silicon respectively. The thick film in Fig. 5 shows loss of adherence during the oxidation–reduction cycle. The 750 Å film on sapphire exhibited superior adhesion.

For the analogous experiments performed at higher magnetic fields a Cahn Model 2000 balance was positioned over a 4 in Varian electromagnet such that an approximately 1 cm^2 sample could be suspended by a combination of nylon thread and fused quartz fiber in a fused quartz tube between the pole faces of the magnet. A Nichrome-wound furnace surrounded the fused quartz tube in the sample region. The bottom of the tube was closed with two thermocouples passing through. The control couple rested on the inside of the quartz tube at sample height while the measuring couple was immediately below the sample. The balance and the sample system were evacuated and back-filled with air to a pressure of about 100 Torr. The magnet was rotated to a position which caused no torque on the sample suspension, i.e. no rotation of the sample which was held vertically. The height of the sample was adjusted to a position yielding a magnetic field gradient of 2.3×10^3 Oe cm^{-1} at a field strength of 9×10^3 Oe. Assuming a detectability of 1 μg, a 1% accuracy of measurement would require an apparent weight gain of 0.1 mg. For cobalt at 350 °C the magnetization (M) is 1.48×10^3 gauss. Therefore, using the fact that the apparent weight is proportional to M, the volume of the cobalt and the field gradient, we find that 3×10^{-8} cm^3 of cobalt can be measured to within 1%. Assuming M is

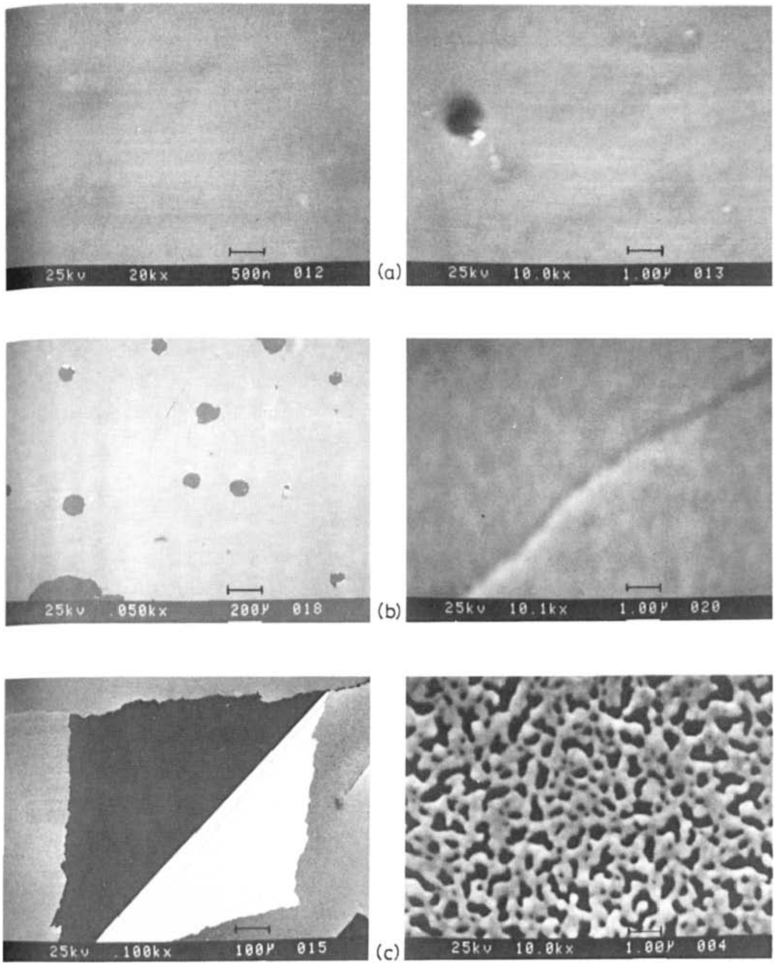

Fig. 5. SEM photomicrographs of a cobalt film 2100 Å thick on single-crystal sapphire: (a) as-deposited; (b) after oxidation; (c) after subsequent reduction.

independent of thickness, this corresponds to only a monolayer on a 1 cm^2 substrate.

For the high field measurements the electromagnet was controlled and the temperature, time and weight were recorded with a Hewlett–Packard data acquisition and control unit. After three temperature and weight measurements, the magnetic field was reduced to zero and the weight in zero gradient was recorded. The zero weight is subtracted from the apparent weight, thereby eliminating the effects of zero drift and changes in buoyancies.

Results are shown in Fig. 7 for the isothermal oxidation of cobalt and lightly oxidized silicon at about 275 °C. The magnetic decay, and hence consumption of cobalt, was observed to follow an exponential decay as

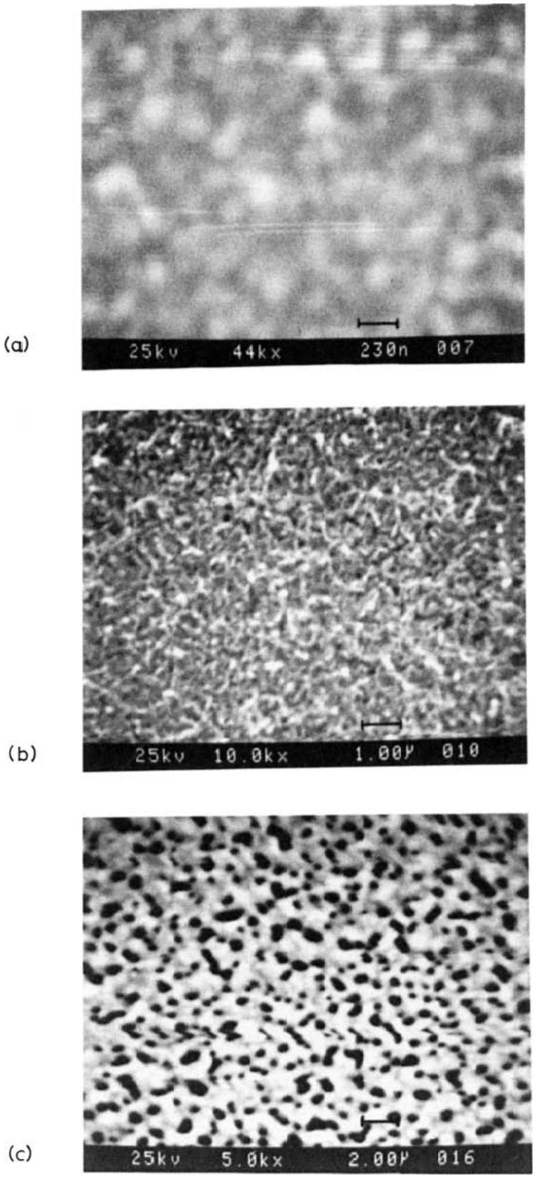

Fig. 6. SEM photomicrographs of a cobalt film 900 Å thick on lightly oxidized single-crystal silicon: (a) as-deposited; (b) after oxidation; (c) after subsequent reduction.

indicated by the plot in Fig. 8 of ln α vs. time, where α equals the fraction reacted over the range between reaching the control point in the temperature program (at 30 min) and 90% completion. The line is the linear least-squares fit (without weighing of points) yielding the equation

$$\ln \alpha = -0.0294t + 0.6933$$

where t is in minutes. The value of the constant indicates that some reaction

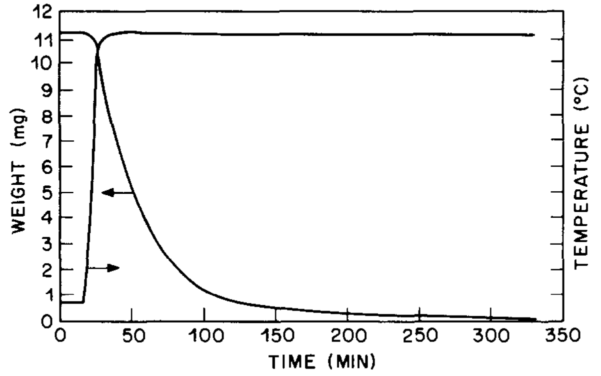

Fig. 7. Isothermal (278 ° C) TM curve for the oxidation of a cobalt film 900 Å thick on lightly oxidized single-crystal silicon (about 60 mm^2).

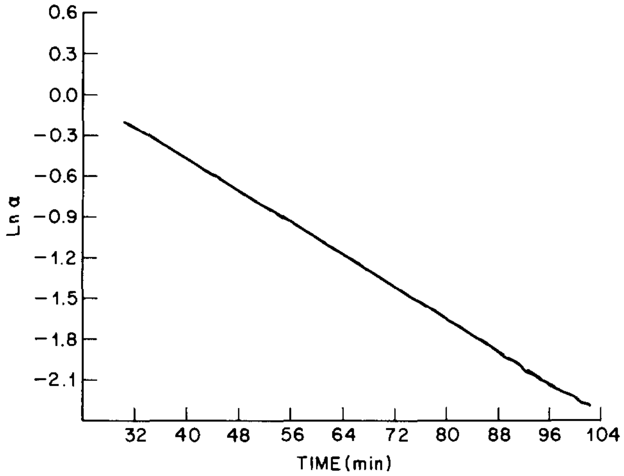

Fig. 8. A plot of the logarithm of the fraction reacted as a function of time for the oxidation of a cobalt film 900 Å thick on lightly oxidized single-crystal silicon at 278 ° C.

occurred during the heating to the control temperature, since the point at $\alpha = 1$ occurs at 23.6 min.

DISCUSSION

The total overall weight gains associated with oxidation of the cobalt films shown in Figs. 1–3 are 2–25 μg. In the presence of the magnetic field gradient from a small permanent magnet, however, the amount of apparent weight change involved in the reaction is multiplied by a factor of more than 300. This makes it feasible to follow the course of such reactions using conventional thermoanalytical equipment with greater convenience and with less complicated methods. In the case of silicide formation shown in Fig. 4, there is no weight change at all associated with the reaction in the absence of a magnetic field gradient. The temperature at which this reaction occurs is severely retarded by the intervening layer of SiO_2, otherwise it would have occurred at temperatures comparable to those of the oxidation reaction [3].

It can also be seen from Figs. 1–3 that the method works equally well for reactions which either consume or form magnetic materials. In order to measure quantitatively the true rate of the reaction, however, it must be established that there are no changes which result in magnetic effects other than changes in the concentration of the product or reactant. Unfortunately, the substantial changes in morphology of the films depicted in Figs. 5 and 6 raise considerable doubts on this matter. During the final stages of oxidation or initial stages of reduction, the magnetic material may be present in such small clusters that they are superparamagnetic and hence not detectable by the technique. Furthermore, since the apparent weight is proportional to the vector magnetic moment $\bar{m}$, any deviation from saturation, i.e. where $\bar{m}$ is parallel to the applied field, may well lead to erroneous results. An applied field that is large compared with any anisotropies present, will remove this source of error in all cases except for particles small enough to be superparamagnetic. In this case a large field only tends to minimize the error.

Working at higher magnetic field strengths which ensure saturation should substantially help to remove some of these uncertainties. The degree of fit to the exponential reaction rate in Figs. 7 and 8 is remarkably good but no mechanistic implications are to be inferred from this single set of data.

CONCLUSIONS

Thermomagnetometry offers a highly sensitive technique for following the consumption or formation of magnetic materials. Even a small permanent magnet in conjunction with conventional thermogravimetric equipment provides a means to follow such reactions involving as little as 1.5 μg of magnetic material or films as thin as 10–20 Å, depending on how much area can be conveniently loaded on a sample pan. Substantially increased sensitivity is possible, with less convenience, using a large electromagnet and some of the potential problems in the interpretation of the data are removed by virtue of using the higher fields to saturate the sample magnetically.

These conclusions were demonstrated by following the oxidation and subsequent reduction of cobalt films on both sapphire and lightly oxidized silicon substrates. In addition, the consumption of cobalt by reaction with the substrate to form a silicide could be followed even when there would be no weight change at all associated with the reaction in the absence of a magnetic field gradient.

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