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Properties characterization and thermal analysis by new thermal constants techniques [1]

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Abstract

Recent new or improved thermal analysis and thermal constants measurement techniques have been developed to evaluate, rapidly and accurately, thermal and related properties of materials available only in small quantities, including thin films, wafers and sheets. These innovative mostly transient techniques can also be used as thermal analysis tools.

Measurements of thermal conductivity, thermal diffusivity, specific heat, thermal expansion and related properties by these methods have been undertaken on a variety of different materials. Results will be presented and discussed to illustrate the use of these techniques for characterization and evaluation purposes. Examples will include metals, ceramics, semiconductors, polymers, and amorphous and inorganic materials measured at different temperatures or ranges of temperature from below 10 K to above 1000 K.

INTRODUCTION

The past three decades or so have seen the measurement of precise thermal properties change significantly from an exercise of predominantly academic interest to a most complex issue employing the attention of scientists and engineers from many disciplines. A vast number of new and improved materials in various forms have been developed for a wide variety of applications. As a consequence of these needs, new and improved methods of measurement have been found necessary to keep pace with the materials explosion.

Several of these newer methods utilize small specimen forms and short measurement times, and are often of higher precision than their more classical predecessors. As a result, they have been found to be useful additionally as qualitative tools, thus providing the thermal analyst with greater flexibility [1].

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In the present paper a number of examples are discussed to illustrate the value of these newer thermal parameters measurement techniques as total characterization and evaluation tools.

THERMAL PARAMETERS

Specific heat by a.c. calorimetry

This high sensitivity technique has been used on a wide range of materials for a variety of applications particularly in the detection and quantification of minute phase transitions, including second- and third-order phenomena [2]. Materials have included polymers, liquid crystals, metals and ceramics especially those exhibiting magnetic, dielectric, ferroelectric and piezoelectric behavior. It has also been particularly useful for studies on superconductor materials at cryogenic temperatures.

In many cases, these multiple transitions can occur at closely similar temperatures and the heats of transition associated with them are extremely small (less than 0.1 kcal mol^{-1}). These levels cannot be detected precisely by DSC or other thermal analysis techniques where standard heating rates of 5–10°C min^{-1} are used and where the degree of precision decreases at lower heating rates. However, in the case of a.c. calorimetry, the high measurement precision is maintained even at heating rates much lower than 1°C min^{-1}. This is due to the sensitivity of the specially developed digital lock-in amplifier used to measure the very small a.c. temperature excursion, plus the use of a platinum resistance thermometer for absolute temperature measurement at the very slow controlled heating rates involved.

A particular example illustrating the use of the technique is barium titanate. This piezoelectric material exhibits a phase change in the region of 400 K with a very small associated heat of transition. Figure 1 shows the

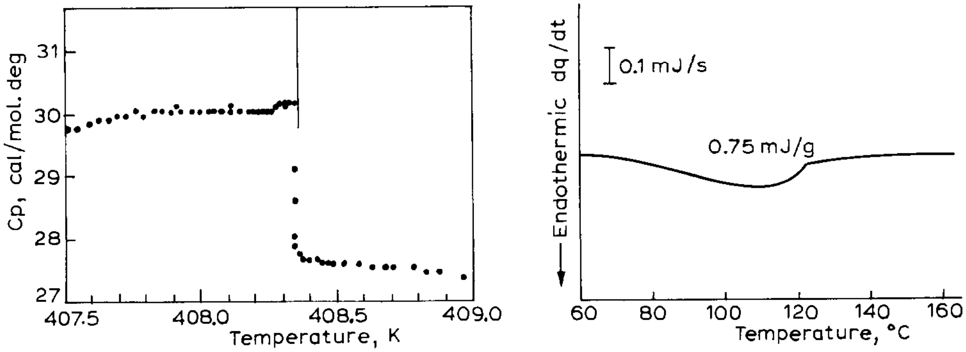

Fig. 1. Measurement of the transition of barium titanate.

results of measurements by a.c. calorimetry and DSC techniques. The former technique indicates that a primary transition occurs at 408.3 K with a heat of transition of 0.05 kcal mol^{-1}, whereas the DSC measurements show only a transition range with an imprecise value of the heat of transition.

Other examples include the following: (i) $NaNO_2$, a dielectric material which has a first-order transition at 337 K from ferroelectric to anti-ferroelectric, with a second-order transition to the dielectric phase at 338 K [2]; (ii) the detection of an incommensurate phase in quartz between the α- and β-phases occurring over a temperature range of less than 0.5 K at 751 K [3]; (iii) the existence of a double superconducting transition at 90 K in $BaYCu_3O_7$, indicating a second superconducting phase similar to the well-known orthorhombic phase [4]; (iv) a means to classify the quality of $BaYCu_3O_7$ superconductor material in terms of the shape of the C_p vs. T curve and the magnitude of the change ("jump") in specific heat C_p/T_c at T_c evaluated from the curve [5].

Thermal diffusivity by the flash method

Since it was first developed 30 years ago, this basic technique, and several variations and modifications based on different and measured analytical models for various applications, have been used for a very broad range of materials and temperatures usually with a laser as the energy source.

In general, its application has been to determine absolute values of thermal diffusivity from which thermal conductivity can be derived. However, there are many cases where the method has also been of great qualitative value. Some examples include measurements to understand how best to (i) increase the thermal conductivity of AlN to levels closer to the theoretical maximum by the addition of different amounts of Y_2O_3 and reduction of total O_2 [6]; (ii) increase the thermal conductivity of ceramics by varying processing parameters in order to increase density, reduce impurities, increase grain size, eliminate or minimize imperfections, grain boundaries, etc.; (iii) decrease the thermal diffusivity of thermosensitive papers to produce improved printing quality in thermal printers and facsimile machines.

A new application we are studying is based on a modified two-dimensional analysis [7]. This has been developed to evaluate larger area, thinner specimens such as 40 mm × 30 mm × 0.6 mm semiconductor or ceramic wafers. The results are best used comparatively although absolute values are possible using reference specimens. Some preliminary results taken with a matrix of nine set positions over the surface of an aluminum nitride wafer and a silicon wafer were encouraging in that reproducible values were obtained at specific positions. For AlN, the results indicated that the wafer had uniform properties. However, for the silicon slice, lower values than expected were obtained indicating the presence of imperfections. Thus the technique has significant future potential for quality control evaluation of the uniformity and homogeneity of materials and layered composites especially for use in electronic packaging.

Thermal diffusivity by a.c. calorimetry

This technique was developed specifically to assist in the characterization of materials and layered structures produced in the form of very thin films, both self-supporting and deposited on substrates. Because the thickness may often be less than the mean free path, the thermal properties of the material can differ from those of the bulk material. Thus for the application it is necessary to know the performance characteristics appropriate to a material and its thickness.

The method provides the materials scientist with a versatile new quantitative and qualitative tool to examine the performance of materials for many different applications. Particular examples include the following.

(i) Superlattice films such as the AlAs/GaAs film used for the clad layer of the surface oscillation diode of the GaAs laser. The films consisted of stacked superlattices built on an easily removed substrate. The thickness range of each layer was of the order of 50–500 Å and the final film thickness was of the order of 10 μm. Results for thermal diffusivity vs. thickness are illustrated in Fig. 2 together with those for GaAs and the $Al_{0.3}Ga_{0.5}As$ compound. It can be seen that the thermal diffusivity of the superlattice film is greater than that of the compound film but smaller than the average of those of AlAs and GaAs. In addition, it becomes smaller as the thickness of each layer is reduced and the period of the two lattices becomes shorter. Further work is proceeding to clarify these differences in performance between the bulk material and superlattices.

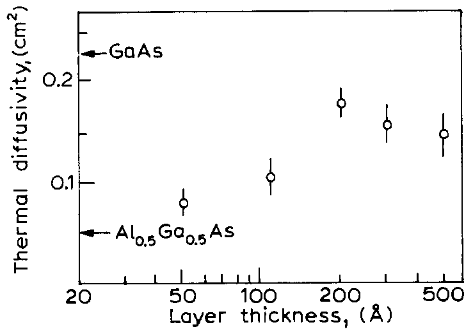

Fig. 2. Variation of diffusivity of AlAs/GaAs superlattices with layer thickness.

(ii) Diamond is an extremely important material because it is both a very good thermal conductor and a very good electrical insulator. Various methods of producing diamond films having different properties have been developed. A means to measure properties is necessary in order to obtain required information regarding the optimum way of producing a film with the required thermal conductivity. A particular investigation on one type of film studied the effects of methane concentration [8]. In this, plasma chemical vapor deposition films, 5–30 μm thick, were deposited on narrow silicon wafers approximately 100 μm in thickness. Results indicated that the methane concentration had a significant effect on the crystallinity and hence on the property of the diamond. As the concentration of CH_4 is reduced below 1% by volume, the structure of the diamond approaches that of the natural material and values of derived thermal conductivity approaching 1000 $W\ m^{-1}\ K^{-1}$ were obtained at concentrations less than 0.2 vol.%. This technique has proven not only of use for evaluating processing effects but can also be used to study local variations in film quality over large areas of a specimen because thermal conductivity is very sensitive to structure differences.

Other current studies include oxide and other ceramic coatings on structural and electronic materials, changes in properties of ion-implanted amorphous and other materials to improve surface characteristics during processing, and analysis of optomagnetic recording films to provide improved performance.

Thermal expansion by laser interferometry

This technique was designed primarily for its ability to provide absolute quantitative data of high precision, especially for specimens having optimum lengths in the 10–15 mm range. Its major applications include (i) provision of reference and standard materials for other less precise methods such as dilatometry; (ii) measurements on low and negative thermal expansion materials ($\alpha \ll 5 \times 10^{-6}\ K^{-1}$) such as fiber-reinforced polymer, metal and ceramic composites, some carbons and graphites, glasses and amber; (iii) quality control and inspection of materials especially where specific matching of expansion coefficients is necessary, such as space optics supports, sealing materials, bimetallic composites and precision electronic instruments.

However, it has also been used on thin films and sheets of materials having higher values of thermal expansion to provide both quantitative and qualitative information on the behavior of materials. For these small specimen configurations, the specimen is sandwiched between either a 15 mm long fused quartz reference piece and one of the mirror plates (thin films) or between two fused quartz rods of total length 15 mm (sheets). By

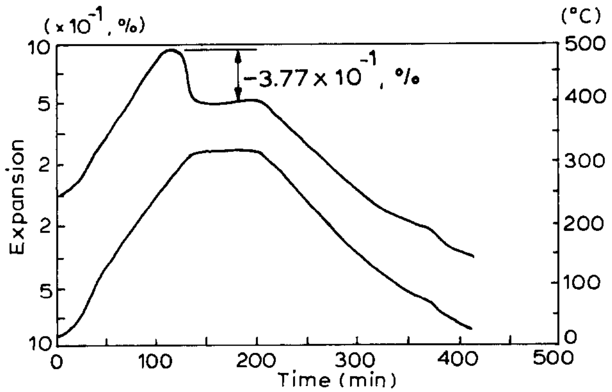

Fig. 3. Thermal expansion of a 0.295 mm thick sheet of a beryllium–copper alloy.

undertaking measurements with and without the specimen in place and subtracting the values, the expansivity of the specimen can be determined.

Figure 3 illustrates the use of this technique for a 0.29 mm thick specimen of a beryllium–copper sheet heated and cooled to approximately 570 K. The alloy consists of a single α-phase up to around 550 K where it changes to a mixture of α- and β-phases. The shrinkage that occurs is due to the precipitation of the β-phase in the supersaturated phase. It is also interesting to note that the specimen length on cooling has undergone a permanent change because the mixed phase remains stable.

SUMMARY

Various thermal analysis applications of some newer quantitative methods, developed originally for measuring thermophysical properties on small specimens, particularly those in the form of thin films, foils and sheets, have been discussed.

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