Note: A variable temperature cell for spectroscopy of thin films
T. Brock-Nannestad, C. B. Nielsen, H. Ø. Bak, and M. Pittelkow

Citation: Rev. Sci. Instrum. 84, 046106 (2013); doi: 10.1063/1.4802949
View online: http://dx.doi.org/10.1063/1.4802949
View Table of Contents: http://rsi.aip.org/resource/1/RSINAK/v84/i4
Published by the American Institute of Physics.

Additional information on Rev. Sci. Instrum.
Journal Homepage: http://rsi.aip.org
Journal Information: http://rsi.aip.org/about/about_the_journal
Top downloads: http://rsi.aip.org/features/most_downloaded
Information for Authors: http://rsi.aip.org/authors
Note: A variable temperature cell for spectroscopy of thin films

T. Brock-Nannestad,1, a) C. B. Nielsen,2 H. Ø. Bak,1 and M. Pittelkow1
1 Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark
2 Sun Chemical A/S, Københavnsvej 112, DK-4600 Køge, Denmark

(Received 13 March 2013; accepted 11 April 2013; published online 25 April 2013)

We report the design and construction of a cell that enables precisely controlled measurement of UV/Vis spectra of thin films on transparent substrates at temperatures up to 800 K. The dimensions of the setup are accommodated by a standard Varian Cary 5E spectrophotometer allowing for widespread use in standard laboratory settings. The cell also fits in a Bio-Rad IR-spectrometer. The cell is constructed with an outer water cooled heat shield of aluminum and an inner sample holder with heating element, thermo-resistor and windows, made from nickel coated copper. The cell can operate both in air, and with an inert gas filling. We illustrate the utility of the cell by characterization of three commercially available near infrared absorbers that are commonly used for laser welding of plastics and are known to possess high thermal stability.

The characterization of thin films has attracted the widespread attention in the scientific community over the past decades. The characterization of mono-layers, as well as thicker spin-coated or drop-casted films has become increasingly important, especially in materials chemistry and nanoscience. Microscopy (e.g., AFM, STM, TEM, and SEM), X-ray diffraction, vibrational spectroscopy (e.g., IR and Raman), and performing optical (e.g., UV/Vis and fluorescence) techniques have been employed in the study of thin films for a plethora of applications.

UV/Vis spectroscopy probes the electronic properties of molecules and the possibility of recording UV/Vis spectra of thin films at variable temperatures is appealing. The techniques can be used for elucidating phenomena not readily investigated in solution, such as molecular aggregation, ring-opening, and degradation. These mechanisms can have a profound impact on the absorption cross-sections of molecules and materials, and thus on the feasibility of given applications.

In the context of synthesizing and evaluating new near-infrared (NIR) absorbing dyes for laser welding of plastic, we have become interested in testing the stability of dyes at high temperatures. Laser welding of plastic is an important emerging industrial process that utilizes near-infrared lasers to weld pieces of plastic together. Laser welding of plastic is typically achieved by incorporating a near-infrared absorbing dye into one of the two pieces of plastic one wishes to weld together. The two pieces of plastic are placed on top of each other and laser irradiation with a wavelength that corresponds to the absorption of the NIR absorbing dye is performed. Laser welding provides a convenient way to make very narrow welding zones as compared to other types of welding procedures. In the typical laser-weld the light is passed through a transparent upper layer, and the energy is absorbed and dissipated in the imbedded lower layer. The heating of the lower layer – most intensely in the upper part – forms a melt zone, where the upper, transparent, layer melts at the interface. The degree of penetration of the two layers depends on the specific polymer. It follows that the ideal NIR absorbing dye for plastic laser welding is colorless in the visible region and absorbs intensely in the NIR region, where the laser of choice emits. The NIR-absorption of the dye is transmitted to the surroundings in the form of molecular vibrations, heating the plastic, and causing welding to occur. For use in industrial laser welding processes, NIR pigments such as Carbon black, various metal-attached phthalocyanines, and more recently, differently substituted rylene molecules are well studied, very chemically inert, heat resistant and often relatively cheap to produce. An issue with most of these dyes is their chemical stability; a stable dye leaves the plastic highly colored after the weld has been made.

Herein we describe our design of a variable temperature (VT) cell to study thin films. We have applied this cell to the characterization of three commercially available NIR absorbing dyes.

The use of variable temperature inserts in absorption spectrophotometers has a long history. The Beckman DU spectrophotometers, one of the standard instruments, build from 1941 to 1976, saw the use of several designs for work with molten salts. Most of these were directed towards measuring in standard quartz sample cells while others were directed towards more forcing conditions, utilizing, e.g., a corrosion resistant liner or designs aimed towards high pressure work. The importance of not heating the sample chamber and the instrument in general has been commented on, corroborating the observation that the instrument should reach thermal equilibrium for high fidelity measurements to be obtained. A further approach has been the design of a dedicated high-temperature instrument.

The current sample design differs from the previous mentioned in that it is directed towards thin film samples, that it is actively cooled on all exterior surfaces, and in that it fits directly in the standard sample chamber of the instrument, and

a)Author to whom correspondence should be addressed. Electronic mail: theisn@kitu.dk.
can be removed as easily as any standard sample holder. The extra set of windows of this design ensures, that the low thermal mass sample is not cooled by convection, and thus allows for precise temperature control, by measurement of the temperature of the heated block. Implementing a PID-controlled temperature regulation, the temperature of the sample block can be held constant to $\pm 70 \text{ mK}$ or ramped. To ensure the highest possible performance, it is recommended that reference beam attenuation be employed during measurement.

The cell is constructed from three major parts; the cooling mantle, the lid, and the sample holder. The cooling mantle and lid are made of aluminum, and provided with interior water cooling channels. The shape of the cooling mantle is cylindrical, and all seals are made with o-rings. The cooling mantle is provided with two windows; o-ring sealed and made of quartz. The sample holder is also cylindrical, made of pure copper, which has been galvanically coated with nickel to enhance resistance towards oxidation. A heating element is wound around the cylinder, the exterior of which is grooved to enhance mechanical contact. The heating element is galvanically isolated from the sample cell, having a protective Hastelloy tube. The heating element is surrounded by a dual layer stainless steel heat shield, which also serves as the anchoring point for affixing the sample holder to the lid. The ends of the sample holder are both closed by unsealed quartz windows, while the sample is placed in a nickel coated holder, positioning the sample in the center of the sample holder. The temperature of the sample block is measured with a Pt100 resistance thermometer, the need for windows being verified by placing a micro Pt100 resistance element where the sample would be, and measuring the temperature between it and the Pt100 resistance element imbedded in the sample block. The lid is provided with a power electrical feed-through for the heating element, and a multi-pole connector for the temperature measurements, both of the hermetically sealed type. Connections to the Pt100 resistive elements are four-wire, and by way of glass-fiber insulated cables. Further, the lid is provided with gas inlet and outlet, to provide the option of using an inert atmosphere. The parts of the cell are schematically shown in Figure 1. In our use, the positioning of the unit as a whole in the spectrometer is by way of a plastic fixture, as the beam-height varies from instrument to instrument. For use in the IR, windows can be changed from quartz to silicon. Both the heating of the sample cell and the temperature
FIG. 5. UV/Vis spectra of Projet NP 950 at various temperatures. The degradation of the NIR absorbing dye was monitored at 940 nm (inset).

reading were controlled by a LabVIEW program, communicating with the power supply and multimeter over a IEEE-488 bus.

Our initial tests have employed the three commercial laser dyes illustrated in Figure 2. These were chosen due to their widespread use and high thermal resistance. The Lumogen dyes are both of the expanded perylene family, while the NP 950 dye is a halogenated phthalocyanine dye. Solutions of the dyes in dichloromethane were spin-cast onto circular cover slides and then placed in the sample holder. The temperature was gradually increased, and absorption spectra were recorded at regular intervals. As seen from Figs. 3 and 4, the degradation of Lumogen 765 is perfectly regular, while the degradation of Lumogen 788 exhibits a thermochromic shift. The Lumogen dyes show the similar qualitative thermal stability. The NP 950 dye, so named for its application at 950 nm is actually an absorber that is better suited for application at 1050 nm. It has significantly reduced stability as compared to the Lumogen family of dyes.

As shown in Figs. 3–5, the variable temperature cell enables the convenient and precise study of the UV/Vis spectra of the three commercial NIR absorbing dyes Lumogen 765, Lumogen 788, and Projet NP 950. The simple experiment also enables the study of the temperature dependant degradation of the NIR absorbing dyes in the thin films. This method compliments other solid-state degradation techniques such as thermogravimetric analysis.

We have illustrated the use of simple and readily fabricated VT cell for medium temperature absorption spectroscopy on thin films of three commercially available NIR absorbing dyes. The size of the cell allows for ready use in most commercial dual beam spectrophotometers.

We wish to thank the University of Copenhagen and the Danish Strategic Research Council through the project “Expanding the weld compatibilities of plastic” for financial support. Further, we thank Mr. Michael Berend and Mr. Jørgen Jørgensen of the Central Workshop at the Faculty of Science, University of Copenhagen for technical support.