

FTIR Spectroscopic Techniques for Quantitative Characterization by Abrasion with Potassium Bromide

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Abstract

In previous methods for the quantitative infrared analysis of solids in KBr (potassium bromide) it has been necessary to obtain pellets of reproducible or known thickness. The infrared spectra in the 5000-370 cm^{-1} (% transmission versus cm^{-1}) region are generally recorded with the KBr pellet method which has some advantages over the mull techniques; absence of interfering bands of the matrix, lower scattering losses, higher resolution of spectra, better control of concentration and homogeneity of sample, possibility of storage of specimens for further studies, so on. Using an internal standard in Nujol mulls which it is not necessary to determine the sample thickness, a quantitative infrared method was developed. There are many analytical methods that are used as physical and chemical characterization techniques for the microelectronics industry. Film thickness has been routinely determined by optical reflectance and ellipsometric techniques and recently by thermal wave measurements. Qualitative IR spectroscopy is a valuable analytical tool that allows for the identification of organic and inorganic materials. Each compound's IR spectrum contains a substantial amount of information. This information, besides some patience, skill, and knowledge about a sample's background, can be used to determine molecular structures successfully, as well as to characterize unknown materials.

Key words: FTIR spectroscopy, KBr, Nujol mull, quantitative

INTRODUCTION

FTIR (Fourier Transform Infrared) technique has been used extensively since three decades. However, arguments still persisted as to whether dispersion instruments still have their place in industrial environments. Now the spectra of coals can be correlated to properties of the coal by a mixture of principal component analysis and multivariate analysis, allowing the accurate prediction of the properties of new samples in a matter of minutes [1, 2]. The other applications are in the petroleum industry. There is an interesting corollary of the widespread application of principal component analysis to infrared spectra, especially true for near infrared. The validity of use of principal component analysis requires that the measurable data are linearly correlated to the property. This implies that the concentration of the chemical species be linearly related to the absorbance. As we are dealing with very complex chemical mixtures in most of these applications this requires that molar functional group absorbances are transferable. It is surprising that many physical properties are linearly related to concentrations of chemical groups. The past thirty years have undoubtedly had a significant impact on routine

spectroscopic practice indeed some of the apparently most obscure instrumental advances today represent highly important elements of analytical instrumentation [3, 4].

In previous methods for the quantitative infrared analysis of solids in KBr (potassium bromide) it has been necessary to obtain pellets of reproducible or known thickness [5]. The infrared spectra in the 5000-370 cm^{-1} (% transmission versus cm^{-1}) region are generally recorded with the KBr pellet method which has some advantages over the mull techniques; absence of interfering bands of the matrix, lower scattering losses, higher resolution of spectra, better control of concentration and homogeneity of sample, possibility of storage of specimens for further studies, etc. [6]. Developed a quantitative infrared method, using an internal standard in Nujol mulls is not necessary to determine the sample thickness. However, quite often the mull spectrum of a substance will be different from its pellet spectrum because the latter may be affected by pressure effects, crystallization, exchange of ions, formation of solid solutions, reactions in the solid state.

In previous works on some thiourea derivatives and

other investigations we were interested in this problem and we adopted the cumbersome method of recording the spectra both with the Nujol mull and the alkali halide pellet techniques, taking from these last spectra only the bands masked by Nujol in the mull spectra [7]. The effect of grinding the sample and the internal standard is the most critical factor involved in the quantitative analysis of solids in potassium bromide. By using an internal standard in potassium bromide the sample thickness is eliminated, thereby simplifying the preparation of calibration curves and the actual analysis. The infrared absorption spectroscopy has long served as a powerful tool in the study of the basic structure and properties of molecules. The analysis of FTIR spectra is greatly facilitated by the fact that certain groupings in molecules give rise to characteristic group frequencies which in most cases are not strongly affected by neighbouring atoms [8].

There are many analytical methods that are used as physical and chemical characterization techniques for the microelectronics industry. Film thickness has been routinely determined by optical reflectance and ellipsometric techniques [9] and recently by thermal wave measurements [10]. The method described in this study has now been generally adopted with satisfactory results. The substance is finely and smoothly ground under Nujol directly on the KBr pellet and the mull gently pressed between two KBr pellets in order to reduce it to a thin and uniform layer. Then recording the spectrum the pellets are carefully separated and Nujol is repeatedly washed with very light petroleum ether leaving the fine powder on the surface of the pellets which are then joined again as a sandwich. Second spectrum on the dry powder is then recorded, normally only in the spectral regions obscured by the Nujol bands.

MATERIALS and METHODS

The intensities of spectral bands are used for quantitative ($\pm 1\%$) and semiquantitative ($\pm 10\%$) FTIR analysis. Because of potential spectral interferences, sample preparation variations, and sensitivity limitations, it is difficult to obtain highly accurate quantitative results with FTIR spectroscopy. Quantitative analysis of organic compounds is much more reliably achieved with chromatographic methods. However, semiquantitative analysis is often sufficient to answer the analysis question. In this case, FTIR has an advantage, because it can readily supply qualitative and semiquantitative analysis results. In order for quantitative calculations to be performed, however, the material must first be identified. The capacity of any component to absorb IR radiation is constant. This capacity is termed its molar absorptivity. Additionally, the intensity of any specific absorption band in relation to another is constant, because the intensity of an absorption band is directly proportional to the rate of change in the dipole moment

of that particular vibration. A large change in the dipole moment of the atoms during a vibration will produce an intense band. Thus, very polar functional groups, such as those containing halogens, will exhibit intense absorption bands. An intense absorption band can also be produced by the presence of multiple functional groups within the molecule, such as CH_2 groups in paraffin wax, that each have the same vibrational energy, such that an additive effect is created.

Table 1. Infrared spectra (cm^{-1}) of thiourea recorded in KBr pellet, as Nujol mull between KBr pellets and on the dry powder between KBr pellets [7].

KBr pellet	Nujol mull	Dry powder	Stewart (Nujol)
3380	3380	3365	3365
3275	3275	3265	3258
3170	3170	3160	3156
3095	3085	3085	3097
2680	2670	2670	2670
1613	1612	1612	1617
1590	1590	1590	-
1472	-	1468	1473
1413	1415	1415	1413
1210	1210	1210	1205
1083	1082	1084	1086
728	729	729	730
630	630	630	629
620	620	630	-
515	515	515	-
485	487	490	486
463	464	470	463
413	413	418	411

All quantitative FTIR analyses are done by comparing the intensity of a specific absorption band, in absorbance units, of the unknown material with the absorbance, or band height, of the same material in a standard of known concentration. In a mixture of materials, the absorbances are additive; thus, the total absorbance at any given wavelength is the sum of the absorptions of the individual components. Therefore, for quantitative analysis of a material, it is advantageous to select an absorption band that is not only characteristic of that material but also isolated from absorption bands due to other materials in the sample. Infrared spectra recorded on dry powder spread over KBr pellets. A comparison of the spectrum of thiourea with those recorded in KBr pellets and as Nujol mulls (Table 1).

The absorbance ratio method was applied to the study of archaeological wood deterioration by Kirillov and Mikolajchuk [11]. Ferrus, Pages, and Diez [12] used quantitative analysis for the examination of kaolin-casein coatings on papers. Other methods, such as the internal standard method used by Biscontin and Volpin for the analysis of calcium oxalate films [13], are also available. Infrared spectroscopy is potentially the ideal optical technique for characterizing dielectric thin film because the strong infrared absorption coefficients of dielectric materials in the mid-infrared region enhance the sensitivity of the FTIR methods. Given that the dielectric thin films are typically supported on silicon wafer substrates, however, interferences or complexities such as baseline drift are often manifested in the measured FTIR spectra of the films. Furthermore, since the samples are

multicomponent solids with molecular interactions and because the band absorptions are sometimes overlapped, the FTIR spectra possess multiple complexities. All of these complexities taken together can complicate the quantitative analysis of the spectra. Bruker Equinox 55 Fourier transform FTIR spectrometer (Department of Physics, METU, Turkey) was used for the IR spectral measurements of these samples with standard natural clay and the spectra were recorded over the range of $5000\text{--}370\text{ cm}^{-1}$ (% transmission versus cm^{-1}). Before taking the spectra measurements of the samples, spectrometer was calibrated with polystyrene and silicate oxide of thickness 0.05 nm .

Infrared spectroscopy provides a relatively direct probe of molecular and submolecular structure via the excitation of vibrational states in molecules, and it allows high functional group specificity over the mid-infrared domain ($4000\text{--}400\text{ cm}^{-1}$). In the last few years, infrared spectroscopy has benefited from the development of highly sensitive, rapid response and low noise detectors. FTIR spectroscopy provides a number of advantages over dispersive IR spectroscopy. For example, FTIR spectrometers provide: (I) very sensitive signal detection due to high optical throughput, (II) rapid scanning due to simultaneous collection of all spectral frequencies, (III) excellent reproducibility of the frequency axis due to use of a laser reference. Together these advantages create a probe that is rapid, noncontact, nondestructive, and highly precise [14].

Baghdadi [15] discussed the effects that the FTIR instrumental artifacts have on quantitative determinations, using the determination of oxygen in silicon as an example. A variety of IR accessories, such as IR external reflection, IR emission, diffuse reflectance, and IR internal reflection (also called attenuated total reflectance-ATR), are available that make IR spectroscopic measurements more versatile (Figs. 1 and 2).

Materials of ATR crystals (IRE elements)

Germanium (Ge); high refractive index, used when analyzing samples have a high refractive index.

Silicon (Si); hard and brittle, chemically inert, is affected only by strong oxidizers, well suited for applications requiring temperature changes as it withstands thermal shocks better than other ATR materials, hardest crystal material offered except for Diamond, which makes it well suited for abrasive samples that might otherwise scratch softer crystal materials, below 1500 cm^{-1} usefulness limited.

Diamond; for analysis of a wide range of samples, including acids, bases, and oxidizing agents, scratch and abrasion resistant, expensive, intrinsic absorption from approximately $2300\text{ to }1800\text{ cm}^{-1}$ limits its usefulness in this region (5% transmission).

For thin films, the ATR spectra (Figs. 3 and 4) are

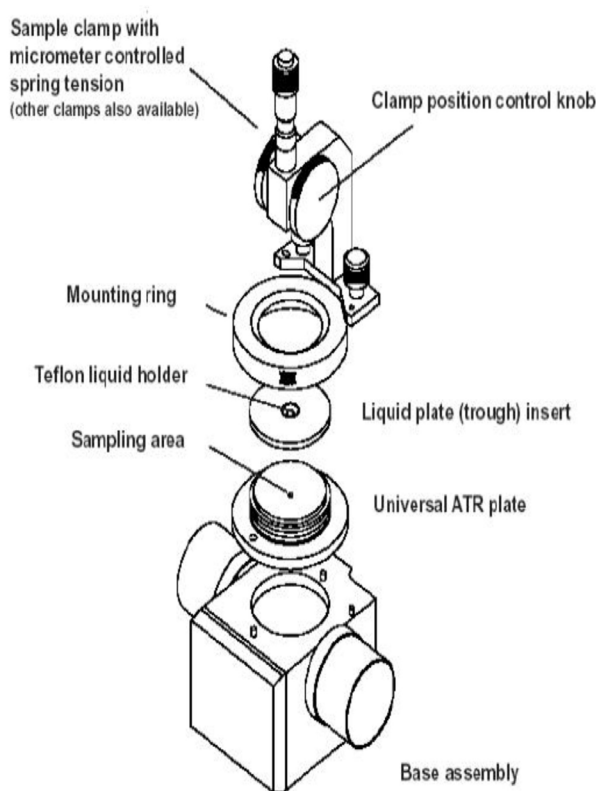


Figure 1. Experimental setup for attenuated total reflectance-ATR.

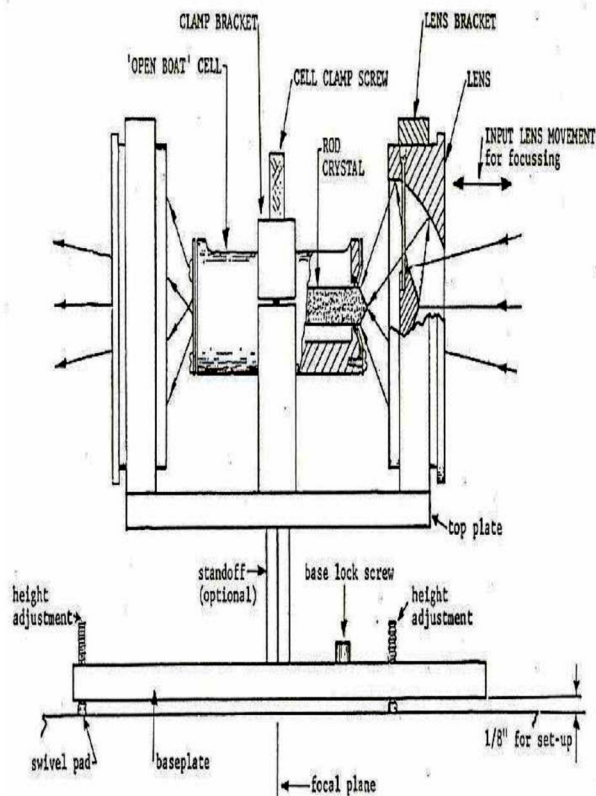


Figure 2. Scheme of the circle ATR cell.

the same as transmission spectra. For thick films, the absorption bands are more intense at longer wavelengths. As the angle of incidence approaches the critical angle, the bands tend to broaden on the long wavelength side and the minima are displaced to longer wavelengths (lower wavenumbers). Dispersion type spectra are observed very close to and below critical angle.

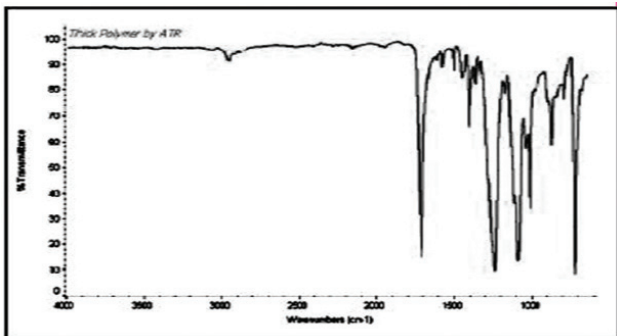


Figure 3. ATR spectra (thick polymer sample, using AMTIR crystal and high-pressure clamp-no sample preparation) [16].

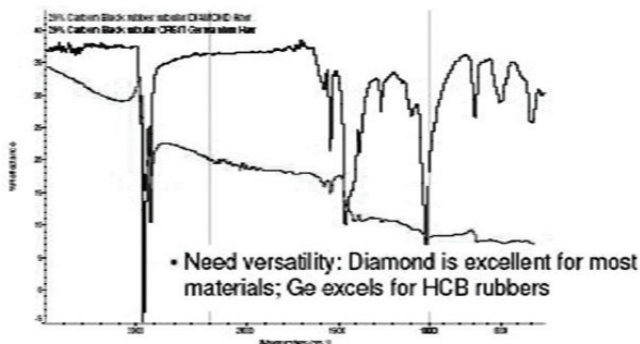


Figure 4. ATR spectra of Rubber-Diamond and Germanium [16].

FTIR spectra were compared with a large number of diverse properties which were measured on the coals, ores, and diesel fuel samples. Where appropriate, the standard methods were applied. Elsewhere, conventional spectroscopic or wet chemistry techniques were used. Spectra of liquid samples were obtained in carbon tetrachloride solution (5% w/v) with the use of a KBr liquid cell of path length 1 mm (Table 2). The same cell containing pure solvent was used to measure a background spectrum [1]. With single-reflection ATR, then, the key is to restrain the sample so that it makes more effective contact with the prism. If necessary, try various measures, such as changing the way the sample is placed or piling multiple samples on top of each other.

Surface Preparation and Reaction Conditions

We had used sodium chloride substrates to develop our technique for using plasma-polymerized films as moisture protective coatings. Unfortunately, this technology on the surface preparation of polycrystalline NaCl was not entirely applicable to polycrystalline KBr.

Table 2. Properties of infrared optical materials.

Material	Transmission Range (cm ⁻¹)	Refractive Index at 1000 cm ⁻¹	Chemical/Physical Properties
Potassium Bromide (KBr)	40.000-400	1.52	Hygroscopic, slightly soluble in lower alcohols, polishes easily
Sodium Chloride (NaCl)	40.000-625	1.49	Hygroscopic, slightly soluble in lower alcohols, polishes easily
Potassium Chloride (KCl)	40.000-500	1.46	Hygroscopic, slightly soluble in lower alcohols, polishes easily
Calcium Fluoride (CaF ₂)	66.666-1110	1.39	Water insoluble, resistant to most acids and bases, soluble in ammonium salt
Barium Fluoride (BaF ₂)	50.000-770	1.42	Water insoluble, soluble in acids and ammonium salt, sensitive to thermal and mechanical shock
Cesium Iodide (CsI)	10.000-200	1.74	Hygroscopic, soluble in lower alcohols
Zinc Sulfide (ZnS)	10.000-715	2.2	Water insoluble, reacts to strong acid, hard material
Zinc Selenide (ZnSe)	10.000-500	2.4	Water insoluble, soluble in acids and strong bases resist to organic solvent
Silver Chloride (AgCl)	25.000-435	1.98	Water insoluble, soluble in acids, will cold-flow, attacks base metals, to UV light sensitive
Silver Bromide (AgBr)	20.000-285	2.2	Water insoluble, soluble in acids, will cold-flow, attacks base metals, to UV light sensitive
Infrared Quartz (SiO ₂)	50.000-2500	1.42	Water insoluble, slightly soluble in bases

We found that commercial KBr could not be polished without large grain domains forming. After grinding by standard methods, various methods of polishing were used on a total of 10 samples. (I) polishing on polytex supreme in isopropyl alcohol, (II) polishing on pitch in ethylene glycol, (III) polishing with black or red rouge on a variety of backing cloths. In no case were the domains eliminated. Furthermore, chemical etching with 48% KBr, which is a method described in the literature for repairing grinding damage at the surface, proceeded at different rates in these domains and the remaining area. We have eliminated the problem by using single crystal KBr.

Surface Passivation

We had found previously that halogen atoms generated from inert Freon gases effectively passivated the surface of NaCl. We believe that halogen atoms replace surface hydroxide groups. One advantage of this method is that it is done under vacuum in the reactor just before the plasma polymerized film is deposited, thus voiding contamination problems. We initially used CF₃Br for the surface passivation of KBr. However, we found that this material caused electrode corrosion, presumably because Br₂ formed in the plasma. As evidenced by their cloudy appearance and large refractive index change, caused possibly by incorporation of halogen, decomposition fragments of CF₃Br, or corrosion products. After the leak was repaired, we found that CF₃Br could indeed be a useful starting material for passivation. Although we did not investigate the specific role of air, we speculate that excited species in the plasma. Also, excited nitrogen or

oxygen could interact with CF_3 radicals to form a species that may be polymerizable in a plasma. We are continuing to optimize conditions for maximum passivation with CF_3Br . During the corrosion problem, we investigated the utility of CF_2Cl_2 for surface passivation. This material did not cause corrosion and did not affect the optical properties of the KBr.

Expansive Stress

In the past, film failure from exposure to high humidity caused by expansive stress was manifested by large cracks in the film. This has not been seen in films on KBr. Therefore, we have not studied annealing or pulse-mode deposition. We will implement these methods, study the relief of expansive stress in the films by annealing and by decreasing the deposition rate using pulse-mode operation.

Thickness Effects

Study related to this task on press unlearn KBr will begin as soon as samples become available. Determine the optimum thickness for adequately coating surface irregularities while having minimum interference with the optical performance of the window. Establish conditions for uniform deposition on both surfaces and edges of a plano-concave structure.

IR Absorption Minimization

Evaluate methods for minimizing absorption in the 8 to 12 μm range by employing reaction conditions that minimize carbon-carbon double bond formation and by removing residual free radicals to prevent the formation of carbon-oxygen functions in the film. Monitor the absorption by FTIR and ATR spectroscopy and by laser calorimetry at 10.6 μm .

Assessment of Progress

Significant progress has been made to date on achieving the objectives of this contract. We are in a position to prepare uniform plasma polymerized films on smooth KBr flats, and we are making excellent strides in the areas of surface passivation and free radical quenching. We will be fine tuning our efforts towards addressing the more detailed aspects of our proposal such as determining optimum thickness for maximum transmission and protection, investigating structure by various spectroscopic studies, and possibly relieving expansive stress.

RESULTS and DISCUSSIONS

Many IR transparent materials are available for use as IR window materials. Each one has certain advantages and disadvantages. Hence and it is up to the analyst to select the material most suited for a particular experiment. The relatively inexpensive KBr and NaCl

windows are commonly used. The KBr and NaCl windows are useful over the entire mid-IR region, but are moisture sensitive and will dissolve in water. Thus, the use of aqueous solutions must be avoided. Moreover, KBr and NaCl pellets, if left in humid air, will fog and become pitted. These windows are, therefore, typically kept in a desiccator. Also, NaCl and KBr windows are easily scratched and gouged, so that the requirement for routine cleaning and polishing makes it hard to maintain the original level of transparency. Poor window surface quality and transparency are particular problems in micro spectroscopy-both during the process of aperture positioning as well as at the photo documentation step.

BaF_2 windows are not taken by water. Therefore, they can be stored in the open, and aqueous solutions can come in contact with the material without dissolution. Also, because the windows are very clear, they provide high-quality imaging for light microscopy and photo documentation. However, BaF_2 windows are roughly four times as expensive as KBr windows. While they can be readily cleaned and polished for reuse, they are also very fragile and will break when dropped even several centimeters. Finally, these windows have a cutoff at 700 cm^{-1} and thus may not be appropriate for the identification of some inorganic materials with characteristic absorptions that occur at lower energies.

Most solid samples can be analyzed as pellets, but it may cause some problems. Nonhomogeneous samples, such as a paint cross section, will be homogeneous after grinding. Since individual components of multicomponent mixtures can be difficult to identify from an IR spectrum, a prepreparation method should be used when feasible. Grinding some samples can cause changes in crystallinity. When particles are not ground finely enough in a pellet, some scattering of the beam may occur, resulting in energy loss and a broadening of the absorption bands. The sample spectrum should always be examined for potential absorption bands due to the pellet matrix, such as water absorption, contaminants, or even reaction products (for example, some organic acids can react with alkali halides).

The comparison of the two spectra (Figs. 3 and 4, and Table 1) shows that the spectrum recorded on the dry powder is highly satisfactory as resolution, sharpness and position of the bands with respect to the other two spectra and that all traces of Nujol have been removed by washing the pellets with light petroleum ether.

Dispersion of particles in an oil mull is a method that has been used for years in IR analysis. Particles are ground finely as for pellets, and then mixed with either a mineral oil (Nujol) or a fluorinated oil (Fluorolube). Since these oils absorb in separate portions of the IR spectral regions, a sample is usually split into two portions, and half is mixed with each type of oil. The mull is spread as a thin film on a salt pellet for analysis. The mineral oil mixture gives a spectrum of the fingerprint region, while

the fluorinated oil mixture provides a spectrum for the functional group region. Because this method is time-consuming and does not have any clear advantage, it is now rarely used, and alternate methods of analysis are preferentially selected.

Reaction conditions have been optimized to yield uniform films on polished and passivated single crystal KBr flats. We found that commercially available polycrystalline KBr flats could not be polished without localized grains forming that could not be removed by chemical etching with HBr. Thickness and transmission are evaluated with each sample. We currently use a thickness of $\sim 5 \mu\text{m}$, which results in a 3 to 5% transmission loss (from the uncoated KBr flat) in the 8 to 12 μm region. In addition to its use in the identification of materials, IR spectroscopy can be used to evaluate the condition of a material and to monitor chemical reactions. Both of these functions are significant to the evaluation and monitoring of deterioration. IR analysis is a very practical method for comparative studies of chemical changes in relation to time and conditions. The measurements made using the spectrophotometer are not particularly complicated, but they do rely on the instrument producing reproducible and reliable results. However, these relatively simple measurements make a significant contribution to a rigorous quality control procedure.

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