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Monitoring Crystallization by Dielectric Spectroscopy

One particularly intriguing aspect of dielectric spectroscopy is its applicability to the studies of systems that undergo chemical and/or physical changes during the application of the electric field, due to, for example, chemical reactions or crystallization /1/. The latter situation is addressed in this communication. Specifically we show how one can follow by dielectric measurements the two principal polarization mechanisms in organic dielectric materials, namely charge migration and dipole orientation, and utilize them to monitor the development of crystallinity and morphology.

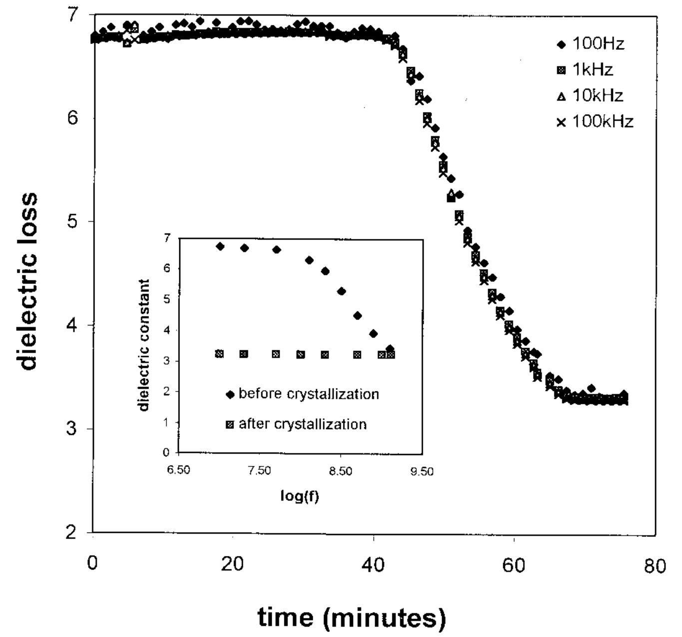

Fig. 1. Dielectric constant as a function of time during crystallization of salol at 26°C. Inset: dielectric constant in the frequency domain in the dipole relaxation range before and after crystallization.

Effect of crystallization on dipole dynamics

The use of dipoles as molecular probes in the studies of crystallization is very attractive because it provides a direct measure of the chemical and physical state of the matter in *real time.* The reorientational dynamics of dipoles can be investigated by dielectric measurements in the frequency, time and temperature domain.

Let us first look at the response of a low molecular weight sample, Salol, that undergoes crystallization. The onset of crystallization at 26°C, following the induction period of circa 40 minutes, brings about a dramatic change in the dielectric response. This is clearly seen in Figure 1 where dielectric constant is plotted as a function of time with frequency as a parameter. The observed drop in the dielectric constant during crystallization is caused by the transformation of amorphous phase into crystals whereby the reorientational ability of dipoles is drastically reduced. A comparison of the dielectric constants of amorphous and crystalline salol (before and after crystallization at 26°C) in the high frequency (Mega and Gigahertz) range of dipole relaxation is added for completeness in the inset in Figure 1.

We next examine a polymer, poly(vinylidene fluoride) or PVDF, and monitor its crystallization by dielectric measurements. There are two ways of conducting such a study /2/: a) by monitoring α_a relaxation, whose molecular origin of is in the segmental motions within the amorphous phase, and b) by tracking α_c peak which is associated with the relaxations within the crystalline phase and whose molecular origin must be sought in the various forms of imperfections that include celiae, discontinuities, etc /3, 4/. The key point here is that, in principle, one should be able to follow the progress of crystallization by monitoring either a decrease in α_a relaxation, as a result of the conversion of amorphous portions into crystals, or an increase in α_c relaxation, caused by the growth of crystalline regions.

Consider α_a relaxation in the melt (200°C) where its dielectric loss peak appears above 10 GHz. Upon cooling PVDF from the melt and allowing it to crystallize isothermally at 155°C (Figure2), we see how the peak intensity *decreases* with time as a result of the ongoing crystallization. An analogous argument, except for the

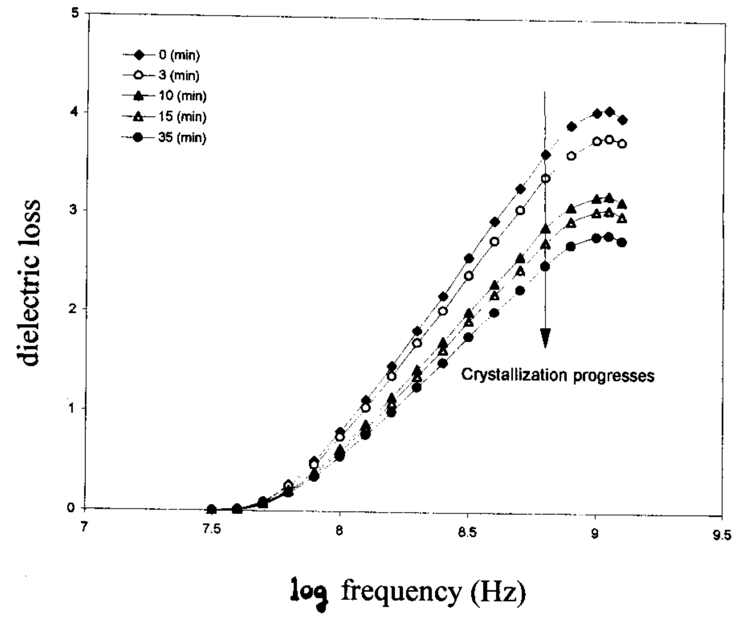

Figure 2. Dielectric loss in the frequency domain, of α_a relaxation during PVDF crystallization at 147°C.

reverse trend, can be made for the α_c peak. In Figure 3, plotted in the frequency domain, we show a gradual *increase* in the peak intensity as a result of isothermal (155°C) crystallization. It is also worth noting that the time scales of α_a and α_c relaxations differ by several decades on the frequency scale. For example, the α_c and α_a peaks at 155°C occur at approximately 100 kHz and 1 GHz, respectively.

We make no attempts here to explore quantitative correlations between dielectric constant and/or loss, on the one hand, and the degree of crystallinity and/or rate of crystallization on the other, though it is apparent that one should be able to correlate a normalized dielectric constant, via phenomenological or molecular models, so some function, say Φ(t,T), that describes the evolution in time of the apparent dielectric constant during crystallization upon the removal of a steady d.c. field from a polarized material. A general expression could be written as:

$$\frac{\varepsilon_t - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \Phi(t,T) \qquad (1)$$

where ε denotes dielectric constant and the subscripts 0 and ∞ indicate initial and final conditions. The frequency-dependent complex permittivity and its time-dependent counterpart are related by a Fourier integral as follows:

$$\frac{\varepsilon_\omega - \varepsilon_u}{\varepsilon_r - \varepsilon_u} = 1 - i\omega \int \Phi(t',T)\exp(-i\omega t)\ dt \qquad (2)$$

where ε_r and ε_u represent the relaxed and unrelaxed permittivity, respectively. The function Φ(t',T) can be also generated by taking Fourier inversion of equation 2, and hence there are various approaches to the analysis of data.

Effect of crystallization on polarization by migrating charges

We now describe how the effect of crystallization on the polarization by migrating charges can be monitored systematically by dielectric spectroscopy. One common graphical representation of data consists of plotting imaginary impedance, Z", as a function or real impedance, Z'. An example of such a plot, known as the Nyquist plot, is shown in Figure 4, which was constructed from a series of sweeps in the frequency domain taken at various times during crystallization of PVDF at 150°C. It is important

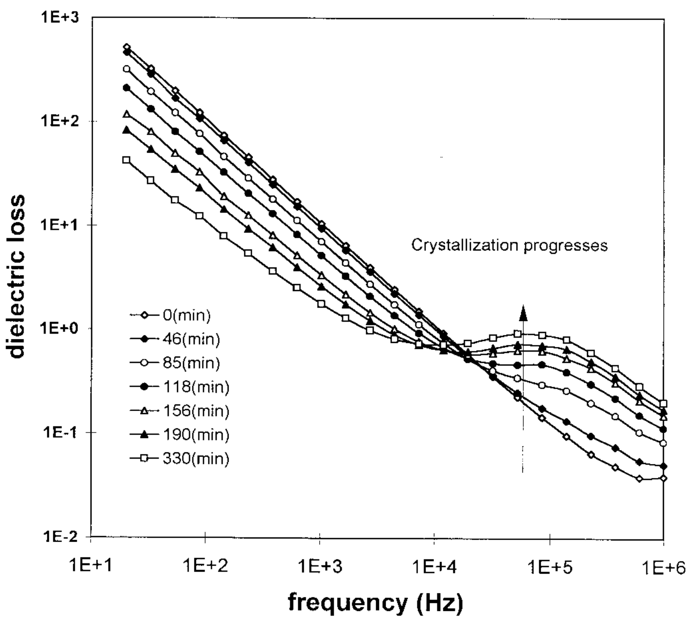

Figure 3. Dielectric loss in the frequency domain of α_c relaxation during PVDF crystallization at 155°C.

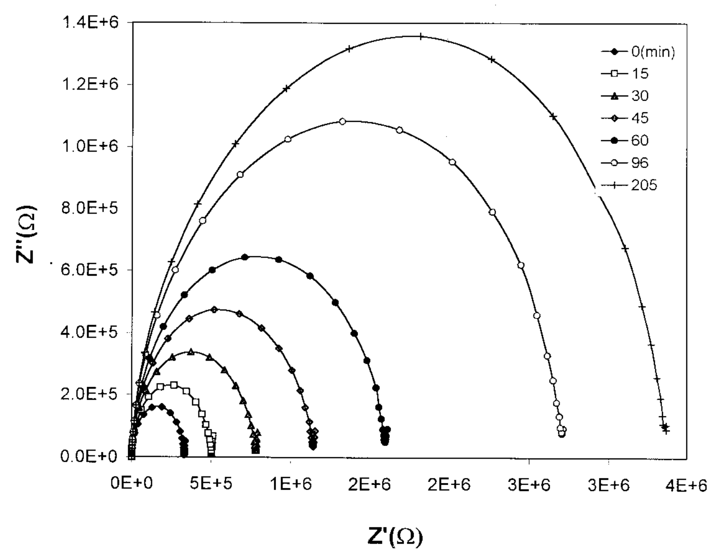

Figure 4. Nyquist plot of imaginary impedance versus real impedance for PVDF with crystallization time at 150°C as a parameter.

to note here that the dielectric response displayed in this figure is not affected by either the electrode blocking layer, which sets in at lower frequencies, or dipole relaxation, which occurs at higher frequencies.

It is also interesting to note that resistivity increases by more than two orders of magnitude during crystallization. Clearly, a normalized resistivity (or conductivity) could be related, via phenomenological or molecular models, to a function, say Ψ(t, T), that describes the progress of crystallization. Fundamental studies of that kind are attractive and warranted, though a host of issues must be addressed beforehand, including the experimental ability to measure high impedance, nonuniform temperature distribution, directional as opposed to random crystal growth, the nature of the migrating charges etc. In conclusion, it is fair to say that dielectric spectroscopy is expected to emerge as an attractive technique for in-situ real time monitoring of crystallization.

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The (Dielectric) Properties of (Ultra) Thin Films

Thin soft and solid films play a dominant role in modern science and technology [1-4]. While the bulk properties of materials are often well explored the influence of the presence of a surface on the structural and dynamic performance of the same material is much less understood. Topological constraints and the interaction between molecules and the surface lead to a complicated interplay resulting in a manifold of surface induced phenomena, such as wetting and dewetting or special molecular conformations. Puzzling is the glass transition of polymers (e.g. Polymethylmetacrylate) in thin molecular layers [5, 6]: Depending on the tacticity of the polymer a shift of the glass transition temperature by more than 60°C is observed! - The technological impact of thin films is not less spectacular. In electronic circuits thin polymeric layers play an essential role as barriers to hinder diffusion of metallic atoms and as low-loss dielectrics to reduce the decay time of miniaturized RC-elements in order to enhance the clock-rate of the whole system [1].

The structural properties of thin films can be studied by a variety of experimental tools, such as scattering techniques (neutron, x-ray, light-scattering) spectroscopic approaches (Fourier Transform Infrared Spectroscopy with polarized light, ellipsometry, fluorescens spectroscopy) or methods allowing for a direct imagination of the surface (scanning probe microscopies, electron microscopies or space resolved mass spectrometry). Concerning the molecular dynamics in the frequency window between 10^{-2}Hz and 10^{10}Hz much less is known. This has a twofold reason:

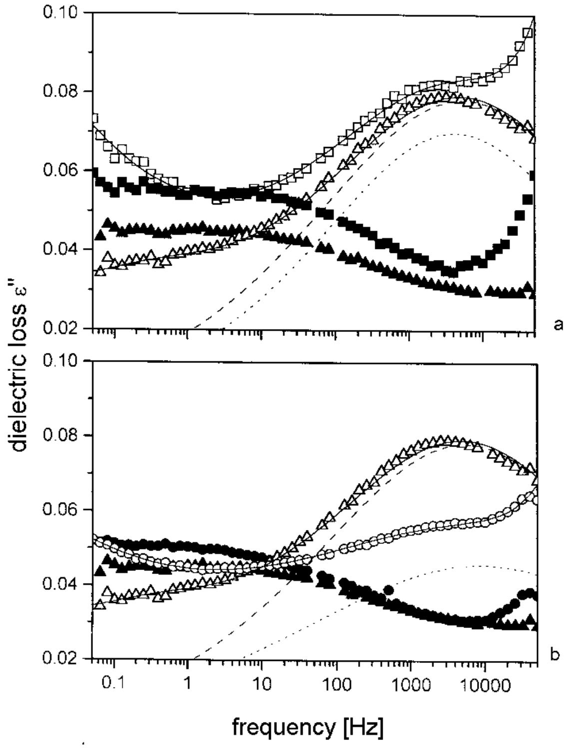

Fig. 1a: Dielectric loss spectra [9] of bulk POMLG (triangles) and a twelve-layer LB film (squares), at 247K (solid symbols) and 267 K (open symbols). For the spectra at 267K the fits (solid lines) are shown. The broken lines indicate the contribution of the major relaxations process.

Fig. 1b: Dielectric loss spectra [9] of bulk POMLG (triangles) and a six-layer LB-film (circles) at 247K (solid symbols) and at 267K (open symbols). Fits as in a).

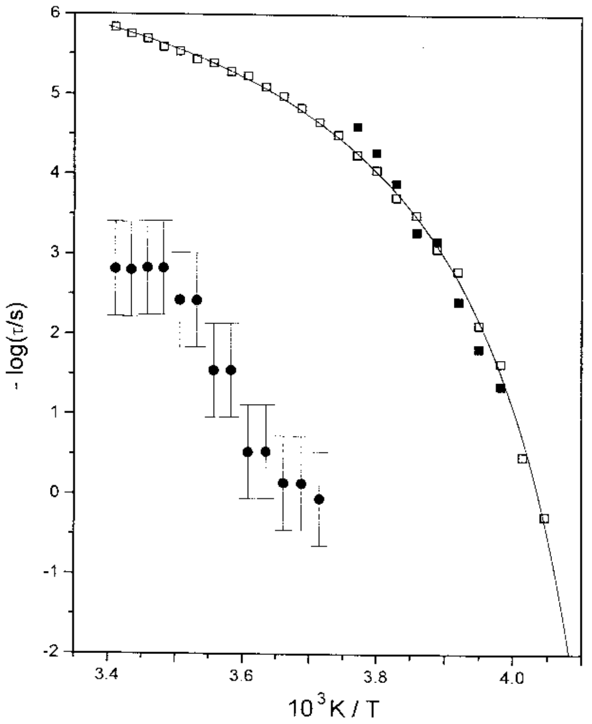

Fig.2 : Activation plot [9] for the two relaxation processes POMLG observed in the bulk sample (circles, open sqares) and the relaxation observed in the six-layer LB sample (solid squares).The solid line indicates a Vogel-Fulcher-Tammann-fit.

Classical methods, like Nuclear Magnetic Resonance Spectroscopy are not able to measure samples being obtained in nanogram quantities; broadband dielectric spectroscopy is faced with the severe difficulty to apply electrical contacts to nm-thick films. To circumvent these limitations of both spectroscopic approaches molecules and polymers being confined to nanoporous media can be employed [7]. This can be very advantageous, but one still has to realize that the nanoporous environment is not comparable to the topology of a flat (ultra)-thin molecular layer.

A few studies exist where the dynamics of polymers in the bulk is compared with that of thin and (ultra)-thin layers [8, 9]. In both cases evaporated gold electrodes were used. This produces especially for (ultra)-thin layers often shorts; furthermore a damage or alteration of the organic layer by the evaporation procedure can not easily be ruled out. In both experiments no significant differences in the properties of the bulk material and the (ultra)-thin layer were observed. In measurements on the "hairy rod" type polymer poly(p-octadecyl-co-methyl-L-glutamate), POMLG, for instance dielectric loss spectra were compared between a bulk sample and a twelve-layer (Fig. 1a) or a six-layer (Fig. 1b) Langmuir-Blodgett film. Within the experimental accuracy no differences could be detected. The difference in the absolute values of ε" can be explained by a 10% error in the determination of the sample thickness. In the activation plot (Fig. 2) the relaxation process having a Vogel-Fulcher-Tammann temperature dependence is practically identical if one compares the bulk and a six-layer Langmuir Blodgett film. A further process being assigned to the molecular dynamics of the polymer backbone is observed in the bulk only.

Dielectric spectroscopy has the principal advantage, that it becomes more sensitive with decreasing sample thickness. This makes it a dedicated spectroscopic tool for the measurement of the molecular dynamics in (ultra)-thin layers in the frequency range from 10^{-2}Hz to 10^{10}Hz. Under the condition that the problem to apply electrodes to a molecular layer can be solved. Skilful experiments are required to overcome this difficulty; if they are successful this would open a broad new field of research activities to dielectric spectroscopy.

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New Developments by Novocontrol

Economical temperature control system Novocool range -100°C .. 250°C

Novocontrol has an excellent reputation as a manufacturer of high quality turn key dielectric spectrometers. An important component of these systems is the temperature control system. Until now, Novocontrol has offered the high class QUATRO Cryosystem and the Novotherm system which are both fully controlled by the Novocontrol software WinDETA for control and evaluation of dielectric and impedance measurements.

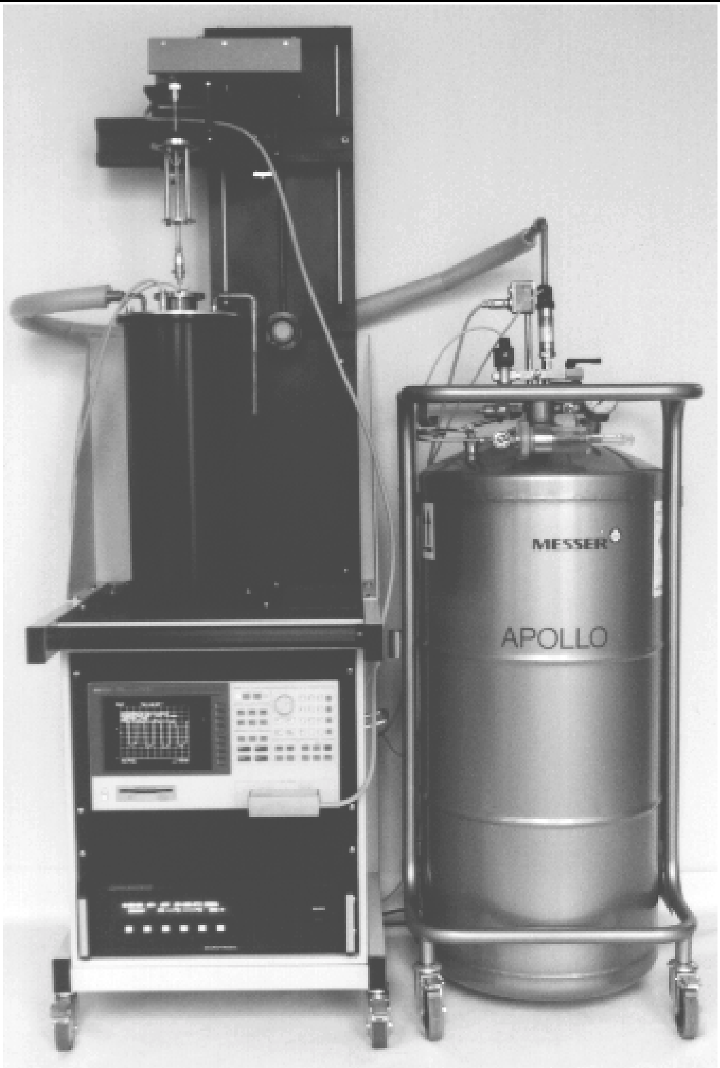

Fig. 1 : Novocool system in combination with the Novocontrol RF spectrometer BDS 60 for frequencies from 1 MHz .. 1.8 GHz and temperatures from -100°C .. 250°C.

The QUATRO Cryosystem offers state of the art performance for even the most demanding scientific applications with 0.01°C stability over a range from -160°C .. 500°C.

The Novotherm is an economical system with 0.1°C accuracy and a temperature range from ambient up to 400°C.

In the last years there has been an increasing demand for an economical temperature control system with an intermediate temperature range. Such a system is available now with the new Novocool system. The temperature range is from -100°C .. 250°C, the accuracy 0.3°C. It is meant for both industrial applications and for scientific applications which do not require the broad temperature range and accuracy of the QUATRO Cryosystem. Like all Novocontrol systems, the Novocool system is modular and therefore can be used in combination with any Novocontrol sample cell and dielectric or impedance measurement system.

The Novocool is based on liquid nitrogen cooling. Liquid nitrogen flows through an isolated line to the evaporator mounted inside of the Novocool cryostat.

The temperature is measured at the lower electrode of the sample cell. In order to optimize temperature control and ensure save operation under any conditions, the temperature of the cold gas is measured with an additional gas temperature sensor. The Novocool cryostat is super isolated and therefore no vacuum is required.

The flow of liquid nitrogen is determined by the pressure inside the dewar. For optimized operation, the dewar pressure is adjusted by the Novocool microprocessor controller. For this purpose a second controller loop is used consisting of the pressure sensor, the dewar heater (to create pressure) and the pressure valve (to release pressure).

A picture of the first Novocool RF system delivered to a leading printed circuit board manufacturer is shown in fig. 1. The system is used both in research and development and quality control.

RF dielectric sample cell with enlarged electrodes for thin film and powder measurements

In addition to the RF sample cell BDS 2100, the new sample cell BDS 2200 is available now.

The BDS 2100 cell is for dielectric measurements from 1 MHz .. 1.8 GHz and temperatures up to 500°C. This cell uses plane capacitor electrodes with diameters from 3 mm .. 6 mm.

The new cell BDS 2200 covers the same frequency and temperature range, but larger electrodes with diameters up to 12 mm can be used. In order to adjust the sample capacity in the same range as with the smaller electrodes, the sample thickness should be increased for the larger electrodes too. E.g. if the diameter is increased from 6 mm to 12 mm, the sample thickness should be selected 4 times the sample thickness of the 6 mm electrode.

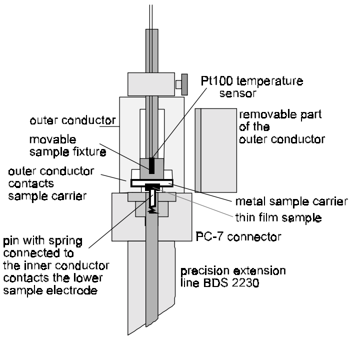

Fig. 2 : Principle arrangement of the new RF sample cell BDS 2200 for electrode diameters up to 12 mm and thin film measurements.

The advantage of using larger and thicker samples is, that the sample preparation becomes easier and more accurate. This is because, if the sample thickness can be prepared with an accuracy of e.g. 10 µm, the relative preparation accuracy will be 10% for a 100 µm thick sample. If instead a sample with 400 µm is used, the relative accuracy increases to about 2.5%.

In addition for the new cell a special set of electrodes for measuring powders is available. In this arrangement the powder is placed in a whole in the lower electrode. This avoids the powder from flowing out of the electrodes.

Moreover, the new sample cell BDS 2200 can be used with a new thin film measurement method. If films below 10 µm have to be measured, the sample capacity becomes quite large if standard electrodes are used. E.g. for an electrode with 5 mm diameter, ε' = 4 and 1 µm thickness, the capacity is about 700 pF which is much to high for measurements at 1 GHz. In order to reduce the capacity into a convenient range of the impedance analyzer (about 5 pF), the diameter has to be reduced to about 0.5 mm resulting in a capacity of 7 pF.

Unfortunately, such small capacitors are hard to prepare with standard electrodes. In addition, due to the small diameter the pressure applied to the film may become quite high if the capacitor is mounted into the sample cell. This is avoided by the set-up for thin film measurements shown in fig. 2. The film is evaporated or grown on the centre part of a 14 mm diameter metal carrier acting as the upper electrode. Then a round metal contact (with e.g. 0.5 mm diameter) is evaporated on the film in order to realize the lower electrode. This structure (metal carrier with film and evaporated contact) is mounted into the RF sample cell BDS 2200 as shown in fig. 2. The metal carrier is connected to the outer conductor of the RF extension line. The inner line conductor is connected by a small pin to the evaporated lower electrode on the film. In order to avoid high pressure on the sample if mounted, the pin is connected by a small spring to the sample.

Improved WinFIT version 2.6

The new version WinFIT 2.6 of the Novocontrol evaluation and non linear curve fitting software for dielectric and impedance measurements is available now. New features are support of the Dissado-Hill functions /1, 2/ for modelling of dielectric spectra. In addition the estimation of the fitting parameters standard deviations is available now for all fit functions.

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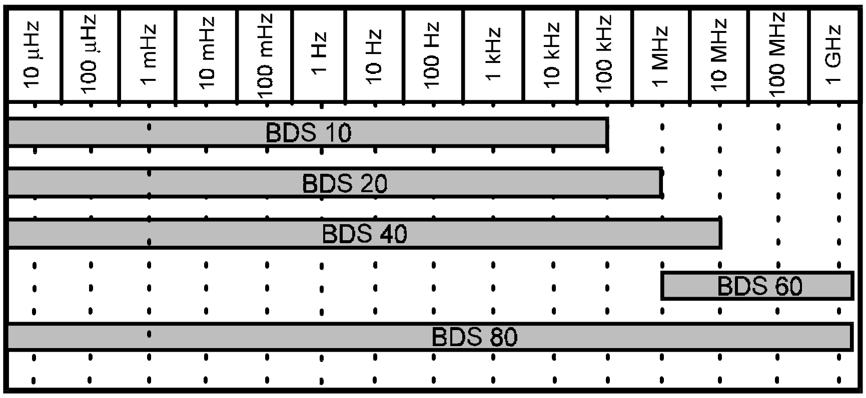
OVERVIEW
BROADBAND DIELECTRIC SPECTROSCOPY
over 15 decades by NOVOCONTROL



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Dielectric Spectrometers and Modules

- ☐ Economical dielectric spectrometers (3 µHz - 100 kHz or 3 µHz - 1 MHz)
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- ☐ RF dielectric spectrometer (1 MHz - 1.8 GHz)
- ☐ Temperature control systems (+20°C .. +400°C or -100°C .. +250°C or -160°C to +500°C)
- ☐ Broadband Dielectric Converter
- ☐ MS-Windows software for automatic measurement of dielectric relaxations, impedance, electrical and magnetic material properties
- ☐ MS-Windows software for automatic curve fitting data analysis (WLF, VF) and equivalent circuit transformation

New Instruments

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- ☐ Pressure dependent dielectric spectrometers

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