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Thermostimulated depolarization currents on a glass surface in ambient gases

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Interdigital comb-shaped electrodes were used to observe thermostimulated depolarization currents flowing on a soda glass surface in ambient gases. The experimental set up, electrode shaping by photograving and measurement procedure are described. Surface thermostimulated depolarization current (STDC) spectra were recorded on glass specimens in dioxide carbon or helium. In both cases, after short gas residence times, depolarization currents were not different from those obtained in vacuum. Different STDC spectra were recorded as the residence time of a glass specimen in CO_2 was increased; these spectra also changed with polarization time and polarization temperature. In helium, STDC peaks were observed at − 110° C and − 90° C with a shoulder at − 65° C. A discussion and an attempt to interpret the results in terms of charge injection in glass involving slow adsorption or absorption of the ambient gas are given.

1. Introduction

The method of thermostimulated currents, widely employed for semiconductors, has been used for about 20 years to study the dielectrical properties of insulators. A study of thermostimulated depolarization currents first enabled us to demonstrate relaxation phenomena of dipoles [1] and then the effects of slow polarization on insulators [2]. Investigations of volume thermostimulation have enabled other researchers to observe the adsorption of vapour (water, methanol) on silica powder [3]. By using IR spectroscopy and RPE methods to observe adsorption on silica [4] or glass [5], other authors demonstrated the existence of physisorption and chemisorption processes. Hence the method of thermostimulated depolarization currents is interesting for observation of the response of a surface (the surface thermostimulated depolarization current, STDC) of an insulator immersed in a gaseous atmosphere (CO_2, He . . .), and to compare these results with those obtained under vacuum in the same conditions.

In a preliminary letter [6], we described the first results obtained with glass in carbon dioxide at a polarizing temperature of 20° C. These results revealed a correlation between the appearance of current peaks during depolarization and the residence time of CO_2 on the solid surface.

In this paper, the experiment is described in greater detail and new results are given. Glass specimens were placed in different conditions, i.e. vacuum, carbon dioxide, a non-polar and strongly polarizable gas, and helium, a non-polar but weakly polarizable gas. In each case, the curves representing the depolarization current as a function of temperature were obtained for two polarizing temperatures, + 20° C and − 20° C. The results obtained are compared.

2. Experimental system and measurement procedure

2. Chamber and sample holder

A cylindrical stainless steel chamber, about 8 litres in volume, held the specimen in a controlled atmosphere, apart from any external influence. The pressure inside could be regulated from a secondary vacuum of 10^{-6} torr to 760 torr of a pure or mixed gas (see Fig. 1). The specimen remained in the upper part of a brass sample holder. Its temperature was controlled by a heating resistance and a cooling pipe conveying liquid nitrogen (see Fig. 2).

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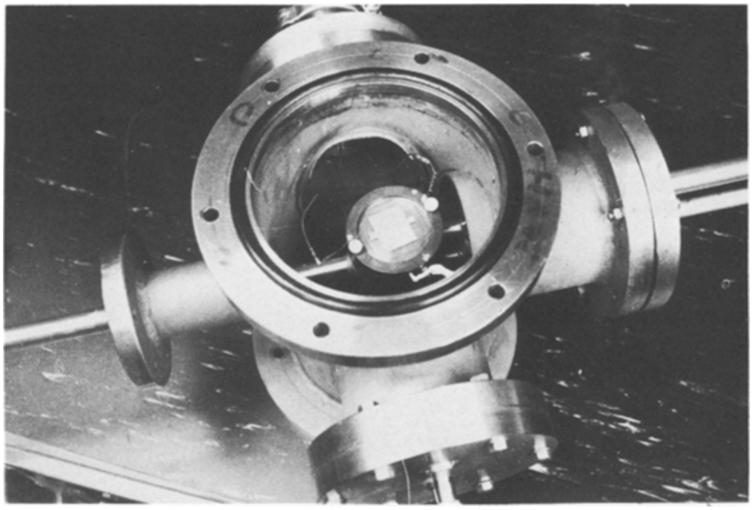


Figure 1 Thermally stimulated current chamber.

The actual material temperature was obtained at any moment by means of a platinum resistance thermometer. This temperature could be raised from $-196°$ C to $200°$ C at a constant rate during each experiment. The heating rate ranged from $0.5°\,\mathrm{C\,mn^{-1}}$ to $8°\,\mathrm{C\,mn^{-1}}$.

2.2. Solid dielectric and gases used

Our specimens were $35\,\mathrm{mm} \times 35\,\mathrm{mm} \times 0.7\,\mathrm{mm}^3$ slides made of window glass with the following composition:

SiO_2, 73%; Na_2O, 13%; Al_2O_3, 1%; CaO, 13%.

The sample was plated on one side with aluminium by thermal evaporation under vacuum (thickness 1000 Å). Interdigital comb-shaped electrodes, as shown in Fig. 3, were then obtained by photograving the surface.

Interpretation of the results can be facilitated by knowledge of the process of this operation. The various stages for each specimen are listed are follows:

(a) Deposition of a positive photosensitive film AZ 1350 on the aluminium plated surface by centifuging at $3000\,\mathrm{t\,mn^{-1}}$ for 15 seconds.

(b) Baking in air at $90°$ C for 15 minutes.

(c) Exposure to ultraviolet radiations on a Microtech 2020 machine for 15 seconds through a mask shaping the electrodes.

(d) Film development in a bath with the composition: Disodium phosphate, 5.5 g; sodium hydroxide, 9.5 g; deionized water, 100 ml. Developing time 15 seconds.

(e) Baking in air at $110°$ C for 45 minutes.

(f) Attack of the aluminium film by a solution including: phosphoric acid, 70%; nitric acid,

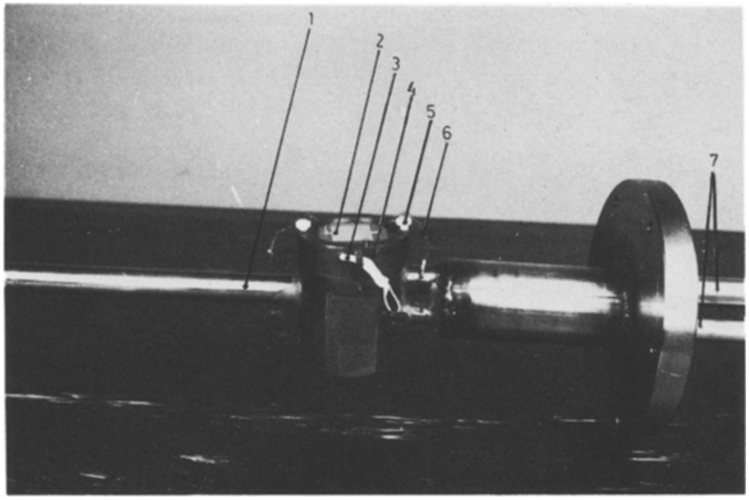


Figure 2 Sample holder photograph showing: (1) pipe housing the heating resistance (2) specimen (3) platinum resistance measuring specimen temperature (4) removable part of the sample holder (5) teflon stand for tungsten spring (6) tungsten spring as an electrical contact to specimen (7) cooling pipe supplying liquid nitrogen.

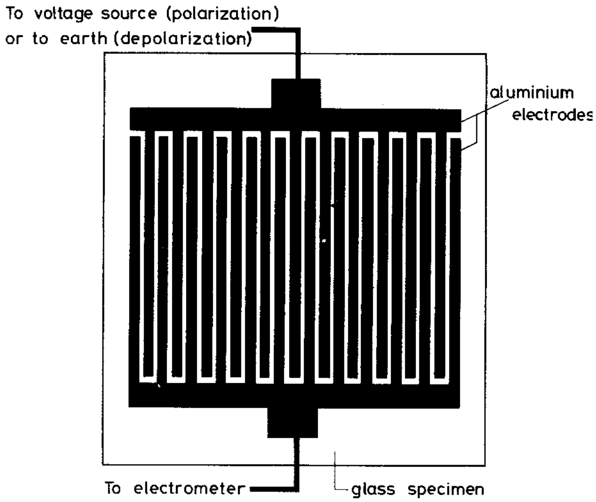


Figure 3 Comb-shaped electrodes.

($d = 1.38$) 3%; acetic acid, 14%; deionized water, 13%.

(g) After photograving, the plates were cleaned by rinsing in abundant deionized water followed by succesive immersion in acetone and in propan-2-ol baths. They were then dried in propan-2-ol vapour.

The stripped glass surface obtained in the polarizable interelectrode by the process described was 16 μm in width and 160 cm in length. The gases used were carbon dioxide (purity 99.998%, $H_2O < 5$ ppm), $O_2 < 2$ ppm, $CO < 1$ ppm, $N_2 <$ 10 ppm) and Helium (purity 99.9999%, $H_2O <$ 0.7 ppm $O_2 < 0.15$ ppm, $N_2 < 0.6$ ppm).

2.3. Electrical circuits for temperature and current measurements

The electrical contacts on both electrodes were made of thin tungsten springs glued on by silver conducting paint. A highly insulated path (insulating resistance higher than 10^9 MΩ) connected one electrode to an electrometer while the other one was connected to a commutator used to polarize and depolarize the specimen.

A Cary 241 electrometer measured the current which was recorded on the y-channel of a Sefram TPR 829 graphic plotter (see Fig. 4).

A platinum resistance was inserted into the sample holder close to the specimen to give its temperature variation. The current through this resistance was kept constant at 0.1 mA, and the voltage measured across it was recorded on the x-channel of the Sefram recorder.

2.4. Experimental procedure

The specimen was degassed by heating at 80° C in 10^{-6} torr vacuum until the residual current became less than 10^{-14} A at 20° C. Then except, of course, for experiments to be conducted in vacuum (10^{-2} torr), the gas was introduced into

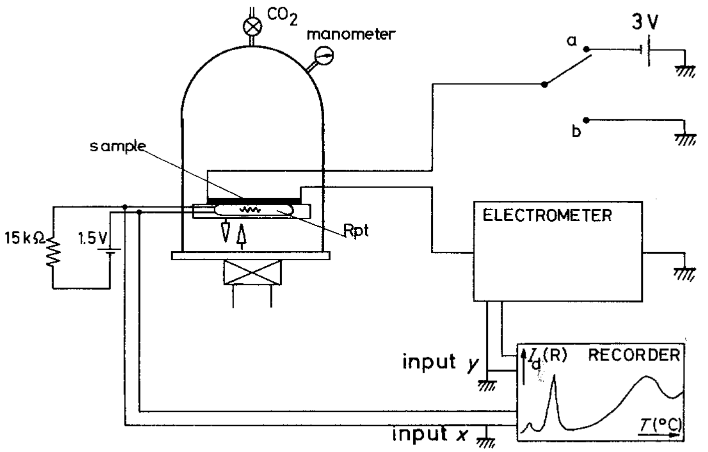


Figure 4 Block diagram of the apparatus used for surface TDC measurement.

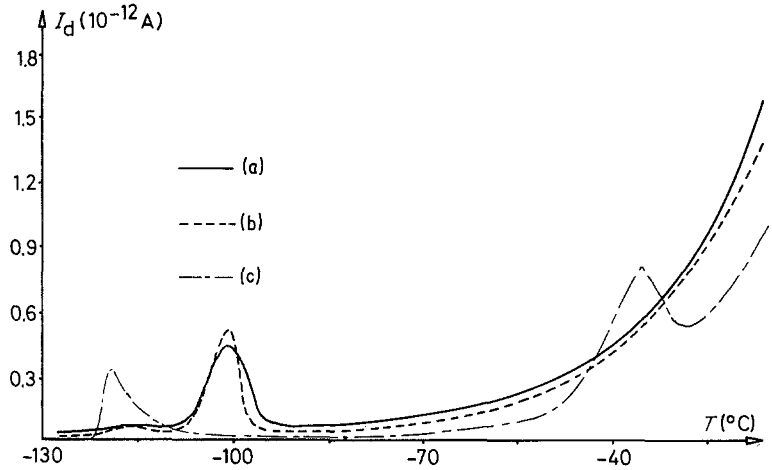


Figure 5 Effect of time and temperature at the surface of the glass specimen in the presence of carbon dioxide under 100 torr pressure. The various STDC spectra were recorded on the same specimen kept in the same atmosphere, (a) after 15 h at 20° C, (b) after 4 hours more at 40° C and (c) after 4 hours more at 80° C ($V_p = 1$ V, $T_p = 20°$ C, $t_p = 1$ h).

the chamber. After time, t_s, a step voltage, V_p = 3V, was applied to the specimen for a time, t_p, at temperature, T_p.

The charge current I_p decreased as a function of time until it reached a stable value (permanent current). The specimen was then cooled to a temperature of about − 150° C. After this operation, the electric field was cut off and the depolarization current I_d recorded, while the sample temperature was increased slowly at a constant rate.

3. Experimental results

3.1. Results obtained with glass and carbon dioxide

3.1.1. Review of results previously obtained at $T_p = 20°$ C

A previous paper [6] described experiments showing the change in electric behaviour of the glass surface in contact with carbon dioxide. These experiments were performed at a polarization temperature of 20° C and a carbon dioxide pressure of 200 torr.

Close similarity was observed between the STDC spectra (current I_d) obtained in vacuum or after a short gas residence time, with a polarization time t_p of 1 hour.

However, with sufficiently long residence times, 15 h for example, another thermostimulated current mechanism took place, due to the continuous presence of the gas. New peaks appeared on the current curve and changed during successive depolarizations (Fig. 5) on the same specimen submitted to different heat treatments in the same atmosphere: during the first depolarization, a peak appeared near − 105° C, whereas in subsequent operations, other peaks appeared near − 120° C and near − 40° C (see Figs. 5 and 6). Hence these initial results revealed changes in the

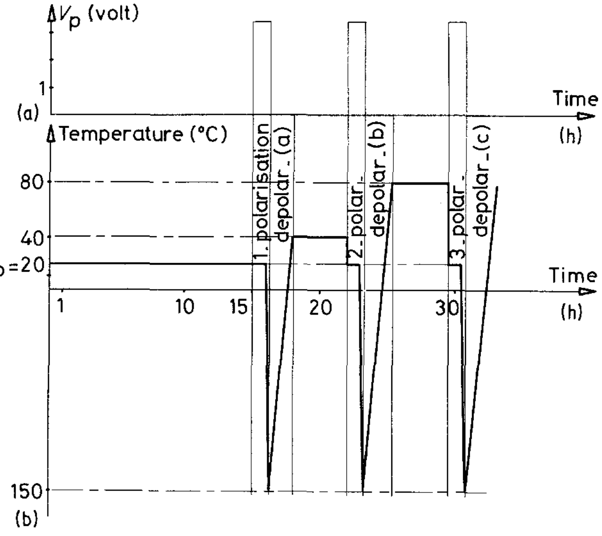


Figure 6 Procedure for the STDC measurements (Fig. 5) as a function of time and temperature (a) bias applied voltage V_p and (b) thermogram.

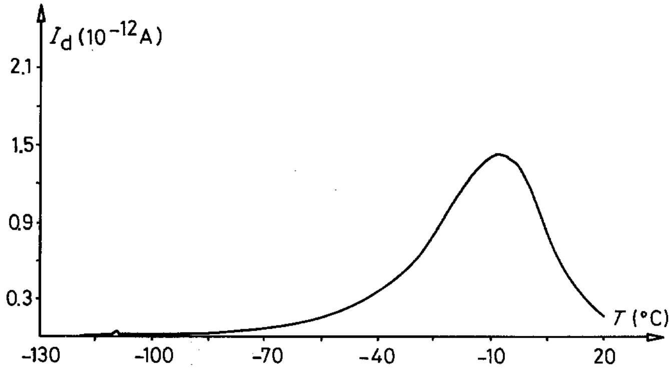


Figure 7 STDC spectra recorded immediately after gas introduction ($T_p = -20°$ C, $t_p = 10$ min, $V_p = 3$ V).

electrical properties of the solid surface and further changes in these properties due to successive polarizations with a predetermined heat treatment in the presence of carbon dioxide.

3.1.2. *New experiments at* $T_p = -20°$ *C*

Before describing the results obtained for this polarization temperature, the following general remark, valid for any polarization time, t_p, should be noted. The current spectra obtained under vacuum and in the presence of CO_2 at $T_p = -20°$ C were different from those obtained at 20° C. A current peak appeared at about − 10° C during depolarization at $T_p = -20°$ C (Fig. 7); however, this is not a characteristic of CO_2 but appears to be associated with the presence of gaseous pollutant in the chamber. In fact, as we shall see later in Section 3.2, an identical current peak was also found in the helium atmosphere.

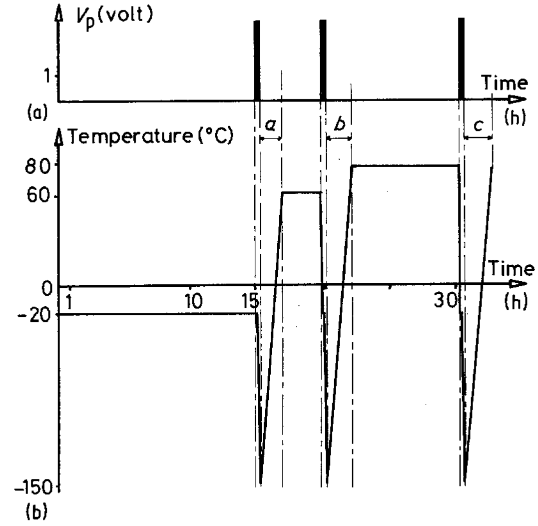


Figure 8 Procedure for STDC measurements (Fig. 9) as a function of time and temperature: (a) bias applied voltage V_p and (b) thermogram.

3.1.2.1. Short polarization time: $t_p = 10$ *min*.

The results presented here were obtained from an experiment involving successive polarizations of the same glass in a CO_2 atmosphere ($p = 100$ torr). Fig. 8 shows the thermal history of the specimens before and during these polarizations. The STDC recorded during the time intervals a, b and c in Fig. 8 are shown in Fig. 9: Curves a, b and c. Fig. 9 elicits the following remarks:

Curve 9a, recorded 15 h after the introduction of CO_2 into the chamber, specimen temperature − 20° C, is similar to the curve of Fig. 7 plotted immediately after the gas was admitted.

Curve 9b corresponds to 22 h of CO_2 residence time, including 3 h at 60° C before another polarization at − 20° C; it shows current peaks at − 120, − 45, − 30 and − 20° C, as well as another peak at − 11° C in the same direction as the polarization current.

Curve 9c was recorded after 30 hours of resident time in the same gas, at 80° C during the last 8 hours followed by a new polarization at − 20° C. Substantial amplification of both the current peaks at − 110° C and − 45° C can be observed.

3.1.2.2. Long polarization time $t_p = 1$ *h*.

These experiments were different from the previous batch not only in polarization time but also temperature and duration of heat treatments between successive polarizations. Considering the importance of polarization time, this new series of experiments should be compared preferably to the first series corresponding to $T_p = 20°$ C but with the same polarization phase duration. The sequence of operations is shown in Fig. 10 and the STDC were recorded during the time intervals marked a, b, c.

Starting from the first polarization (a) which began about 16 hours after introduction of the

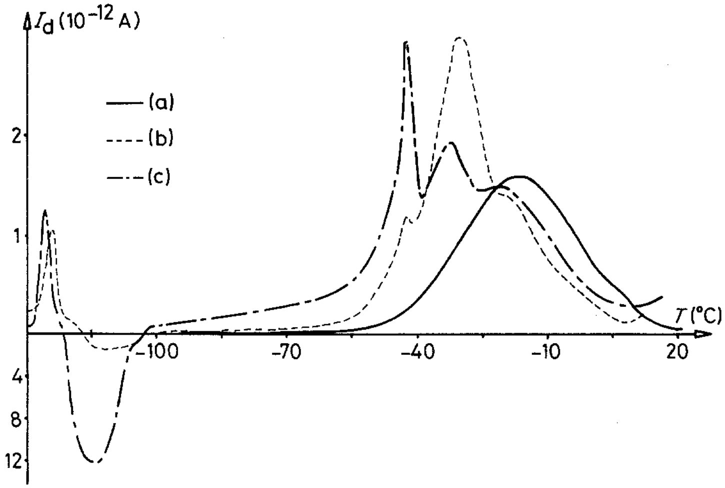


Figure 9 Effect of time and temperature at the surface of the glass specimen in the presence of carbon dioxide (100 torr). The various STDC spectra were recorded on the same specimen kept in the same atmosphere: (a) after 15 h at $-20°$C (b) after 3 hours more at 60° C, and (c) after 8 hours more at 80° C. ($V_p = 3$ V, $T_p = -20°$ C, $t_p = 10$ min).

gas, a current peak appeared at $-105°$ C (Fig. 11a) in the depolarization spectrum. This appears to be a characteristic for the same duration, whatever the polarization temperature T_p. On the other hand, the peak at $-15°$ C was also observed as T_p was always negative (Figs. 7 and 9).

After keeping the sample at 60° C for 4 hours following the previous depolarization and after a new polarization at $-20°$ C, we recorded the depolarization curve shown in Fig. 11b. In this curve a current peak appears near $-115°$ C whereas the peak at $-103°$ C decreases substantially.

At the end of this second operation the specimen was heated at 60° C for 14 h, then polarized at $-20°$ C. The depolarization curve shows a very strong amplification of the current peak near $-115°$ C, while the peak at $-105°$ C emerges out only as a shoulder. Other peaks appear also at -50, -35 and mainly at $-20°$ C.

3.2. Results obtained with glass and helium

Similar experiments were performed with helium filling at 200 torr. The results presented below were obtained with a polarization temperature of $-20°$ C.

When helium was introduced into the chamber immediately before a description, the specimen was not perturbed by the gas apart from a depolarization peak at $-10°$ C. This peak appears to be independent of the composition of the gas as already mentioned in the experiments with CO_2. We must emphasize that it is also found when sample degassing is insufficient.

The first polarization occurred 40 h after helium introduction. Peaks were observed at

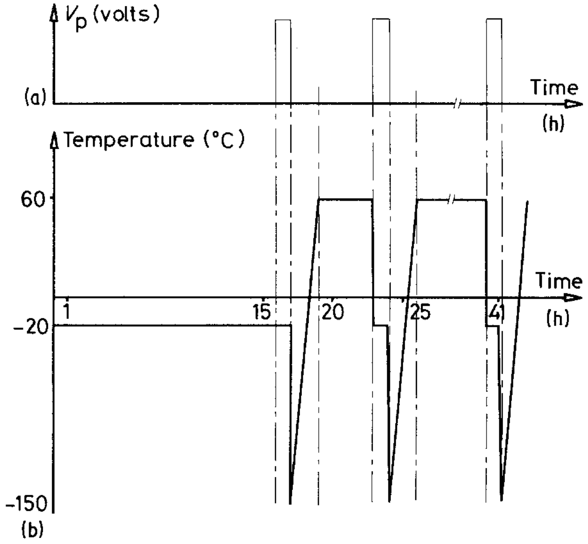


Figure 10 Procedure for STDC measurements (Fig. 11) as a function of time and temperature: (a) bias applied voltage V and (b) thermogram.

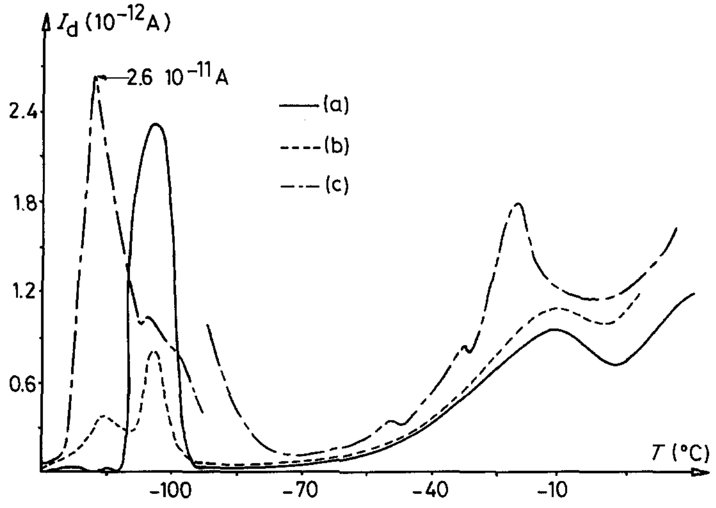


Figure 11 Effect of time and temperature at the surface of the glass specimen in the presence of carbon dioxide (100 torr). The various STDC spectra were recorded on the same specimen kept in the same atmosphere: (a) after 15 h at − 20° C (b) after 4 hours more at 60° C and (c) after 14 h more at 60° C. ($V_p = 3$ V, $T_p = 20°$ C, $t_p = 1$ h).

the following temperatures during the depolarization: − 110° C, − 92° C, with a shoulder at − 65° C (Fig. 12). The successive depolarizations carried out after different heat treatments do not alter these characteristics except for a strong amplification of the peak at − 110° C (Fig. 13).

4. Discussion and attempted interpretation of our experimental results

4.1. Glass–CO_2

4.1.1. Synthesis of the results

The series of experiments concerning the behaviour of a glass specimen in a CO_2 atmosphere points out important physico-chemical processes affecting the dielectric surface.

For the following discussion, it will be useful to refer to Table I which lists the main results described above and indicates the positions of the STDC peaks by an arrow. After short gas residence times (15 min to 1 h), the depolarization currents obtained are not, in fact, different from those obtained under vacuum: The first experiment corresponding to $T_p = + 20°$ C shows that no change occurs in the dielectric properties if the residence time is short. However, the experiments at $T_p = - 20°$ C in CO_2 with a very brief residence time contradict the results obtained at $T_p = +$ 20° C, since a current peak is observed at − 10° C. This current peak does not appear in vacuum unless the sample is poorly degassed or some gas is present, so that it cannot be characteristic of CO_2 but rather of a pollutant.

On the other hand, with a substantially long residence time (e.g. 15 h) a current peak appears near − 105° C, for polarization temperatures $T_p = + 20°$ C as well as $T_p = - 20°$ C, provided the polarization time is 1 hour or more. This implies a very slow gas adsorption or absorption at the glass surface: this interaction between the gas and the solid alters the dielectric properties

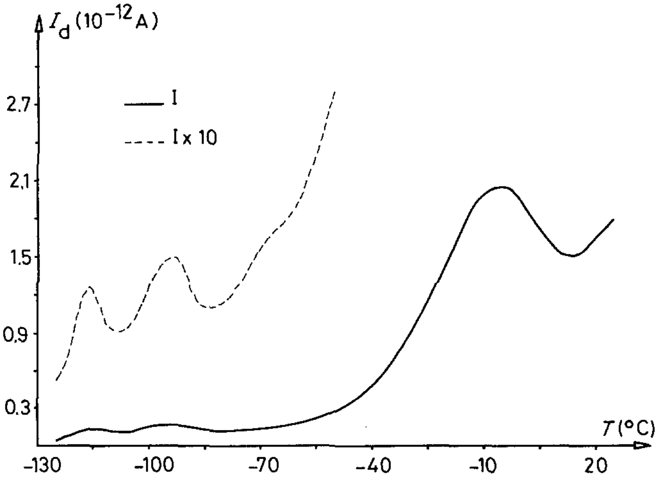
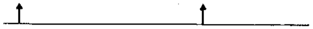
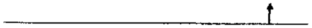
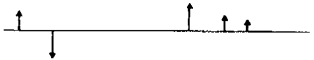
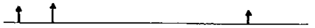
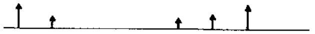


Figure 12 STDC spectra recorded in the presence of helium after 40 h at 60° C ($T_p = - 20°$ C, $t_p = 1$ h, $V_p = 3$ V).

TABLE I Main results and positions of STDC peaks

Polarization T_p (° C)	Polarization t_p (mn)	No. depolarization	Resident time (h)	Thermal treatments time	Thermal treatments (° C)	Depolarization temperature (° C) -120 -100 -80 -60 -40 -20 0	Remarks
20	60	1	1				Spectrum ≡ that obtained under vacuum
20	60	1	16				appearance of a peak at – 105° C
20	60	2	23	4	40		appearance of a peak at – 120° C
20	60	3	30	4	80		disappearance of the peak at – 105° C and appearance of a peak at – 40° C
– 20	10	1	0 h 10				this peak reveals the presence of pollution
– 20	10	1	~ 15				same one as previously
– 20	10	2	~ 22	3	60		appearance of a peak at – 110° C in the same direction as the polarization current (positive polarity)
– 20	10	3	~ 33	8	80		strong amplification of two peaks at – 110° C and – 40° C
– 20	60	1	17				appearance of one peak at – 105° C
– 20	60	2	25	4	60		appearance of two new peaks at – 115° C and – 20° C
– 20	60	3	42	14	60		appearance of two new peaks at – 50° C and – 20° C

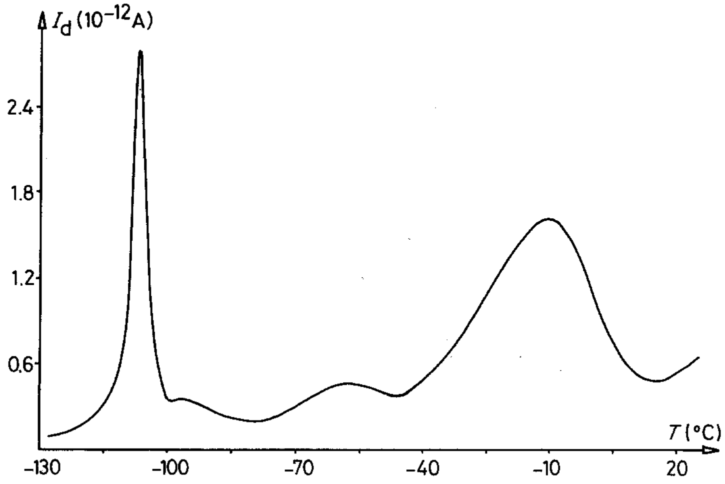


Figure 13 STDC spectra recorded in the presence of helium after many depolarizations ($T_p = -20°$ C, $t_p =$ 1 h, $V_p = 3$ V).

of the surface. As shown in STDC spectra following successive polarizations (Figs. 6 and 11) variations are conditioned either by temperature or duration or even by both these characteristics of the heat treatment.

The results obtained with short polarization times (10 min) seem to be different from those corresponding to longer durations (1 h). No current peak appears near − 103° C and, as successive depolarizations occur a negative peak appears and increases near − 110° C. However a peak is found at about − 120° C, increasing with the thermal cycles and recalling the events in the same temperature range in the experiments with long polarization time on the slope of the STDC spectra. The remaining current peaks have practically the same positions as in the other experiments, but their relative intensities are different.

4.1.2. Attempted interpretation

Slow adsorption or absorption is most probably the cause of the STDC recorded. This hypothesis is confirmed by the fact that no depolarization current indicating the presence of gas appears if the residence time remains short. Consequently, the change in phase sublimation (solid–gas) of CO_2, which takes place near − 100° C, cannot alone explain the peaks observed.

Due to its composition, the glass used includes some oxides and impurities capable of facilitating chemisorption processes, but, it is certainly the actual surface and not only the structure and chemical composition of the material, that seems to be really investigated and responsible for the processes observed. The treatment sustained by the specimen when the metal is deposited may modify its surface. The different chemical treatments used for etching the electrodes may also disturb the interface. However a temperature range exists where no current peak is observed when the specimen is tested in vacuum and only the presence of the gas gives rise to the STDC flowing in the glass surface in this temperature range.

One acceptable hypothesis explaining this kind of gas–solid interaction may be the trapping of electrical charges injected from the electrodes into deep traps created by a chemical complex formed between the gas molecules and some element of the solid material [7]. It is also conceivable that the electrical charges injected into the glass enhance the fixation of gas molecules inside the specimen as charged complexes.

Under the action of heat, the complexes formed could be converted into others having a more stable chemical structure. This could explain the STDC variations as a function of heat treatment.

4.2. Glass–helium

Initially, the fact that the gas is non-polar and weakly polarizable would imply that it might only produce a weak interaction between glass and helium. Yet the STDC observed indicates the occurrence of this mechanism on a relatively broad scale.

As in the case of CO_2, injected charges can be trapped in deep potential wells, but it is difficult to imagine that chemisorption can occur with helium. Hence another explanation must be found.

One possibility is that the presence of an absorbed or adsorbed gas would assist charge transport. Another is that the gas could help to reveal defects in the solid surface: for example, by reducing the rate of fast movements of dipoles or free charges on the surface, by a steric effect.

4.3. Influence of heat treatment

Particularly in the case of carbon dioxide, we have seen the importance of the temperature at which the substrate is held during its residence in the ambient gas. In all gases examined, a specimen residing at a given temperature, T, for time, t, in a gas, g, gives a TDC curve which we call s.

If we place the same specimen in vacuum at moderate temperature (around 100° C for 2 hours) and then, after polarization, record its TDC curve we obtain a result different from s and similar to i, recorded at the very beginning of its residence in the gas. The interaction established between the gas and the surface molecules have been destroyed by the moderate heating, which agrees with our hypothesis of absorption of adsorption of the gas at the surface justified by our measurements.

If we again replace the same specimen at temperature, T, for the same duration, t, in the same gas, g, after polarization we obtain a similar curve to that of s but with the amplitudes of the peaks diminished. Another moderate heating in vacuum followed by polarization would again give the curve i. Another residence of the same specimen in the gas in identical conditions as before would, after polarization, give a curve similar to that of s but the peak amplitude would diminish again and so on.

If a specimen is kept in vacuum at 180° C for 4 hours, after polarization its TDC curve is identical to i, and it will keep this from regardless of any residences in a gas imposed on it afterwards.

These observations show that the specimen surface is modified by heating in vacuum and the higher the temperature the quicker the modification. A structural modification does not seem likely as the vitreous transition temperature of the material used is around 450° C. On the other hand, it is conceivable that the interaction mechanisms observed take place between the gas and the impurities deposited on the surface or the imperfections of this surface, and that heating at 180° C eliminates them. However, the chemical photograving treatment necessary for the fabrication of measurement electrodes may itself be not unrelated to the presence of some of these defects.

5. Conclusion

Our experiments show that the thermostimulated currents of a solid surface depend directly on the ambient gas, and the interaction phenomena between the two phases appears to be a function of the solid's residence time in the gas.

The study of a glass surface reveals the great influence of some parameters such as gas composition, temperature polarization time and heat treatments applied to the material.

Concerning interpretation, the occurrence of STDC peaks only after minimal residence time, shows that absorption or adsorption is involved. However, the differences between the gases used, carbon dioxide and helium, regarding their dielectric properties and chemical reactivity, do not allow only one interpretation of the results for the time being. On the other hand, the chemical compositions and impurities of the glass open up many possibilities of a precise understanding of the mechanisms involved. Hence this work will be continued using materials with a more defined composition and structure such as pure silica and quartz. Some well known defects will be introduced into the surface, making it possible to evaluate the relative influence of these defects and of the substrate itself. The number of variable parameters will also be reduced and their values standardized in our experiments. However, even though all the mechanisms involved are not yet clearly understood, STDC may be used for surface investigations because they offer a very sensitive and reproducible method of characterization. They seem to provide a valuable tool for the study of gas solid interfaces, an area in which experimentation and measurements are particularly delicate.

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