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# Ellipsometric characterization of surface freezing in Ga-based alloys

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## Abstract

We present results on surface freezing of Ga-based alloys, GaBi, GaPb and GaTl, above the liquidus line between the Ga-rich eutectic and the monotectic point. Spectroscopic ellipsometry ( $0.8 \text{ eV} \leq h\nu \leq 4.2 \text{ eV}$ ) and kinetic single wavelength ellipsometry ( $2.75 \text{ eV}$ ) have been employed to probe the changes of the interfacial electronic structures on surface freezing. To minimize thermal gradients across the sample a heatable cap that covers the sample and crucible was developed. The surface freezing temperature,  $T_{\text{SF}}$ , for the spontaneous formation of a solid-like film on top of the Ga-rich liquid on cooling the sample from the homogeneous phase region was found to be independent of the temperature difference between the upper and lower furnace ( $\Delta T$ : +10 to  $-10 \text{ K}$ ) and only weakly dependent on the cooling rate ( $\partial T/\partial t$ :  $2.5\text{--}20 \text{ K h}^{-1}$ ). In the case of GaPb the solid film consists of solid Pb with a thickness  $h \geq 400 \text{ \AA}$ . Comparing with GaBi we draw analogous conclusions for GaPb and GaTl and suggest that the surface freezing transition precedes the bulk phase transition along the liquidus line as the alloy is cooled.

## 1. Introduction

Surface freezing is a rarely observed interfacial phenomenon. In pure liquids it is manifested by a solid-like layer on the liquid surface at temperatures above the triple point. Among the best studied examples are long-chain  $n$ -alkanes. Here the formation of an ordered solid-like monolayer at the bulk liquid/vapour interface has been characterized in detail by surface tension measurements [1, 2], x-ray scattering [3, 4] ellipsometry [5] and various molecular dynamics simulations [6, 7]. Although surface freezing and surface melting are mutually exclusive, both phenomena seem to be symmetrical about the triple point with respect to their respective film thickness variation. This is indicated by a recent grand canonical lattice gas calculation [8].

In metallic fluids, surface freezing has not been reported until now, with the exception of a few Ga-based alloys. A first investigation of a dilute alloy of Pb in Ga has been reported by Rice

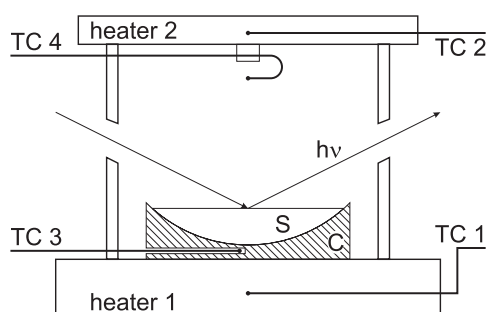
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*et al.*, who probed the liquid/vapour interface by x-ray reflectivity and grazing incidence x-ray diffraction [9]. These measurements indicate a two-dimensional freezing of a Pb monolayer on top of the bulk liquid alloy. The authors also report that the Pb monolayer forms an ordered hexagonal phase which undergoes a first order transition to a hexatic phase at 58 °C and remains stable up to 76 °C [9], i.e. ~46 °C above the eutectic temperature [10]! In subsequent experiments we have studied the GaBi alloy, whose bulk phase diagram is similar to that of GaPb. At compositions between the eutectic and monotectic points we found clear indications of a surface freezing transition whenever the homogeneous liquid alloy was cooled towards the liquidus line. The transition was detected by different spectroscopic methods such as second harmonic generation (SHG) [11], surface light scattering [12], and x-ray photoelectron spectroscopy (XPS) [13], and was also found in a model calculation of surface phase transitions in GaBi alloys [14]. First attempts to measure the thickness of surface freezing films by XPS have been performed recently [15]. They yield lower limits of  $h > 100$  Å for GaBi and of  $h \geq 20$  Å for GaPb. The bulk phase diagram of both alloy systems is characterized by a liquid–liquid miscibility gap [10, 16]. The respective surface phase diagrams are marked by complete wetting transitions at liquid–liquid coexistence down to the monotectic point [17–20]. As a consequence of this wetting transition a Bi-rich or Pb-rich layer exists at the liquid/vapour interface of the bulk liquid alloys; see also [14] and [21]. Therefore it has been suggested that surface freezing in these alloys is due to nucleation of these wetting films which are strongly undercooled with respect to the corresponding bulk phases [22].

From the existing experimental data as sketched above it is clear that surface freezing in metallic systems is far from being understood. Some observations like those of surface freezing film thicknesses are controversial. In a recent publication on wetting phenomena in GaBi the interplay between tetra point wetting and surface freezing has been discussed by Huber *et al* [19]. These authors raise several objections to the occurrence of surface freezing in these alloys. One question is if surface freezing really occurs at thermal equilibrium conditions. It is further argued that on cooling below the monotectic temperature the surface regularly becomes both rough and rigid, but this is interpreted as the formation of bulk solid Bi [19]. This effect should be exacerbated by the presence of temperature gradients and by rapid cooling. In the present study we try to answer part of these questions. First, we were interested in controlling the effects of temperature inhomogeneity and cooling rates and, in particular, in following the surface freezing transition while cooling at constant composition of the alloy. Here is a clear difference from all measurements of Pershan's group [19, 21] which were always taken on cooling along the liquidus curve where both temperature and composition vary. Finally, we employed spectroscopic ellipsometry which promises a distinction between surface film solidification and bulk solidification. For reasons of comparison we have studied the surface freezing behaviour in three alloy systems: GaBi, GaPb and GaTl.

## 2. Experimental details

The ellipsometric experiment has been described in detail elsewhere [20]. In brief, an *in situ* phase modulation ellipsometer (UVISEL, Jobin-Yvon) is attached to a UHV chamber ( $p < 10^{-9}$  mbar). It allows measuring the ellipsometric angles  $\Psi$  and  $\Delta$  at a constant angle of incidence of  $\Theta = 71.2^\circ \pm 0.05^\circ$ . The complex dielectric function  $\varepsilon = \varepsilon_1 + i\varepsilon_2$  of the sample can be derived directly from the complex reflection ratio  $\rho = \tan(\Psi) \exp(i\Delta)$ , employing a two phase model (bulk sample/ambient medium). On the other hand the thickness of a surface film can be calculated in the framework of the three phase model (bulk/film/ambient) if the optical properties of the bulk and the film are known [23]. The spot size of the collimated light beam was about 1.5 mm in diameter. Thus, the illuminated area on top of the sample is about 5 mm<sup>2</sup>.



**Figure 1.** Sample cell with lower heater 1 and upper heater 2. TC 1 to TC 4: NiCr–Ni thermocouples. S: sample, C: Mo-crucible. The temperatures of heater 1 and heater 2 can be controlled separately.

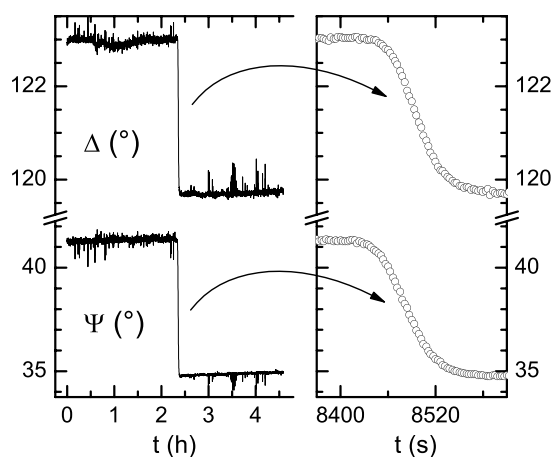
All handling of the samples was done in an Ar glove box ( $O_2$ ,  $H_2O < 1$  ppm). High purity metals (Ga 99.999 99%, Bi 99.9999, Pb 99.9999%, Tl 99.999%, with respect to metallic impurities) were filled in Mo crucibles and the samples were then transferred into the UHV chamber. The diameter of the sample was 40 mm and the total mass of the sample typically between 30 and 35 g. To remove residual impurities the surface of the alloys was further cleaned with an Ar-ion sputter gun and, finally, with a tungsten-wire cleaner [20, 24]. As a result we obtained a clean, flat and highly reflective, mirror-like sample surface. Ga alloys prepared under similar conditions in a UHV chamber equipped with an Auger electron spectrometer were found to be oxygen free at the surface [15].

Special attention was focused on the control of the temperature gradients across the sample. Therefore we constructed a heatable cap which was mounted above the sample. It is shown in figure 1. To fulfil the black body conditions as well as possible, only two circular borings ( $\varnothing = 10$  mm) for the incoming and the reflected beam were left open. The cap could be removed from the sample under UHV conditions with a wobble stick. The temperatures of the lower heater 1 and the upper heater 2 could be adjusted independently (NiCr–Ni thermocouples TC1 and TC2). This allowed for a well defined and reproducible vertical temperature difference  $\Delta T = T_{TC2} - T_{TC1}$ . The temperature of the sample (TC3) was measured with a thermocouple in the centre of the crucible bottom. The temperature homogeneity inside the cap was determined by three additional thermocouples, of which we show only TC4 in figure 1. The absolute accuracy of the temperature measurement was  $\pm 1$  K. Relative temperature shifts could be recorded with a resolution of about 0.02 K.

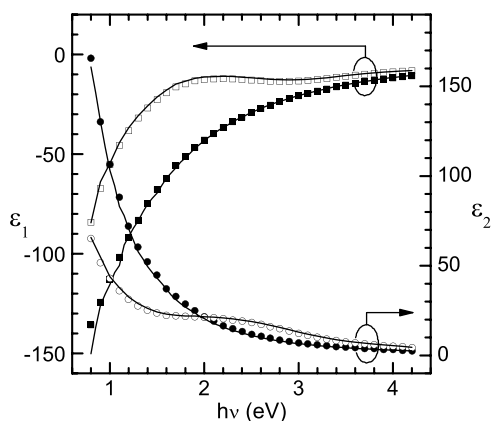
Spectroscopic ellipsometry was performed in the accessible energy range (0.8–4.2 eV) at constant sample temperature. Time dependent measurements were carried out at constant photon energy at 2.75 eV while the sample was continuously cooled or heated. The absolute accuracy for the measured quantities  $\Psi$  and  $\Delta$  were  $\pm 0.1^\circ$ , and the reproducibility was better than  $0.05^\circ$  almost in the entire energy range. To study the surface freezing phenomenon systematically the cooling (heating) rates were varied from 2.5 to 20  $K h^{-1}$ . The vertical temperature difference was varied from  $\Delta T = -10$  K (top colder than bottom) up to  $\Delta T = +10$  K.

### 3. Results and discussion

A typical cooling curve for GaPb is shown in figure 2, where  $\Psi$  and  $\Delta$  are plotted as a function of time. When the temperature reaches about 189 °C the ellipsometric angles exhibit abrupt



**Figure 2.**  $\Psi$  and  $\Delta$  at 2.75 eV of  $\text{Ga}_{0.9944}\text{Pb}_{0.0056}$  as a function of time while the sample was continuously cooled down from 203 to 188 °C with  $5 \text{ K h}^{-1}$  and  $\Delta T = 0 \text{ K}$ . The jump indicates the appearance of the solid surface film at 188.7 °C. The right part shows a 'slow-motion' of the jump.



**Figure 3.** Spectra of  $\epsilon_1$  (squares) and  $\epsilon_2$  (circles) of the free liquid surface (closed symbols) at 203 °C and the liquid surface covered with a solid film (open symbols) at 188 °C (sample:  $\text{Ga}_{0.9944}\text{Pb}_{0.0056}$ ). Solid lines refer to independent measurements of pure liquid Ga and solid Pb at corresponding temperatures.

changes by several degrees. A closer look shows that these changes in the area of the footprint of the light beam occur on the timescale of 1 min. This is in good agreement with previous visual observations of the occurrence of a solid film on GaBi: there, the solidification sets in at the border of the sample and moves as a proceeding front over the entire surface of the liquid sample within several minutes [11]. The important difference in the present experiment is that the sample was covered with the heatable cap and the temperature difference was set to  $\Delta T = 0 \text{ K}$ ! Thus, all temperature gradients across the sample are minimized. In addition, it has to be emphasized that the process occurring at the surface is spontaneous. Thermodynamically this defines a path towards a lower free energy of the system.

To identify the chemical nature of the film we recorded ellipsometric spectra (and show them in figure 3) of the real and imaginary part of the dielectric function at 203 °C when no film is present (filled symbols) and immediately after the jump at 188 °C (open symbols).

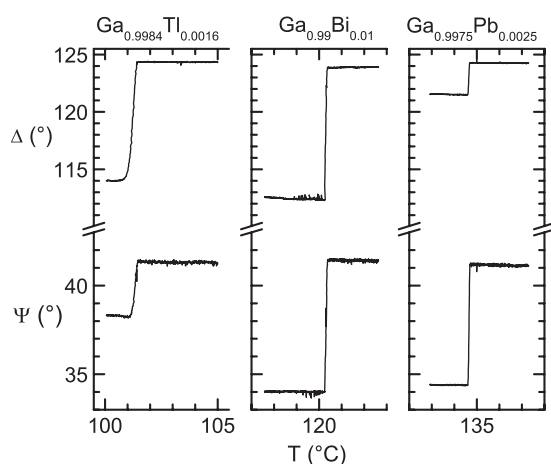
**Table 1.** Surface freezing temperatures  $T_{\text{SF}}$  for  $\text{Ga}_{0.9944}\text{Pb}_{0.0056}$  and for  $\text{Ga}_{0.99835}\text{Tl}_{0.00165}$  for various cooling rates and temperature differences  $\Delta T$  between upper and lower heater.

$\Delta T \rightarrow$	GaPb, $x_{\text{Pb}} = 0.0056$			GaTl, $x_{\text{Tl}} = 0.00165$		
	-10 K	0 K	+10 K	-10 K	0 K	+10 K
Cooling rate ( $\text{K h}^{-1}$ )	$T_{\text{SF}} (\text{°C})$			$T_{\text{SF}} (\text{°C})$		
2.5	188.6	188.9	189.2	103.1	103.8	103.5
5	188.6	188.6	188.7	102.9	103.2	103.2
10	188.0	188.2	188.4	102.4	101.6	102.2
20	187.8	187.4	187.8	101.4	101.2	101.4

The dielectric function has been evaluated from the ellipsometric angles using the two phase model. The spectra at 203 °C are compared to pure liquid Ga at a similar temperature [20]. It is not surprising to observe quantitative agreement since the composition of Pb is very low. However, a microscopic adsorption of Pb at the surface is expected on account of the lower surface free energy of Pb in comparison to Ga [22, 25] but, in contrast to x-ray reflectivity, spectroscopic ellipsometry performed at a liquid surface is not sensitive to a monolayer. The  $\varepsilon_1$ - and  $\varepsilon_2$ -spectra at 188 °C are compared in figure 3 with the respective spectra of pure solid Pb. Surprisingly the agreement is quantitative within the experimental uncertainties. This enables the following conclusions. (i) The film consists of solid Pb. It shows the typical energy dependence in the spectra arising from the band structure of solid fcc Pb [26]. The dispersion changes clearly as Pb melts. It is then a good example for a free electron metal [27]. (ii) Only a lower limit for the solid Pb film thickness can be estimated. Since the spectra of the film and pure solid Pb are almost identical the film cannot be thinner than approximately 400 Å. Spectroscopic ellipsometry in the accessible energy range probed here is sensitive for the thickness of a solid Pb film above liquid Ga roughly between 5 and 400 Å. This has been tested by modelling the ellipsometric spectra within the three phase model assuming a film of pure Pb. The surprising high thickness of the Pb film shows clearly that surface freezing observed in this experiment has to be distinguished from the ordering transition within the Pb monolayer reported by Rice and co-workers [9].

An important objective of the present investigations was the characterization of the conditions under which the surface undergoes the surface freezing transition. Various cooling experiments on a GaPb sample ( $x_{\text{Pb}} = 0.0056$ ) and on a GaTl sample ( $x_{\text{Tl}} = 0.00165$ ), respectively, have been collected in table 1. The surface freezing temperatures,  $T_{\text{SF}}$ , measured in the bottom of the crucible at TC3 (see figure 1) are listed for various cooling rates and temperature differences between the upper and the lower heater ( $\Delta T = T_{\text{TC2}} - T_{\text{TC1}}$ ). It is not surprising to observe a weak temperature dependence on the cooling rate. This is due to the finite heat transfer rate between the crucible bottom and the surface of the alloy. Most interesting is the absence of a significant dependence of  $T_{\text{SF}}$  on  $\Delta T$ ! The surface freezing temperature is highly reproducible within a few tenths of a kelvin, regardless of the fact that the upper furnace is 10 K colder or 10 K hotter than the lower furnace.

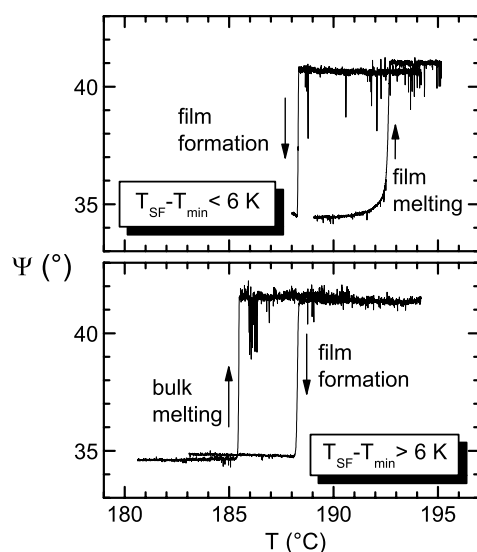
Our previous experiments to study the surface freezing process have been performed without the heatable cap and, thus, the surface of the alloy was exposed to the room temperature environment of the UHV chamber [11–13]. This gave reason to the objection that the transition might be a phenomenon driven by temperature gradients [19]. To exclude temperature gradients as far as possible, the control of the thermal conditions was thoroughly improved. The results summarized in table 1 suggest that the surface solidification phenomenon does not depend on temperature gradients as a driving force.



**Figure 4.** Formation of solid films on liquid Ga-based alloys while the samples were continuously cooled down: GaTl ( $x_{\text{Tl}} = 0.0016$ ), GaBi ( $x_{\text{Bi}} = 0.01$ ), GaPb ( $x_{\text{Pb}} = 0.0025$ ).  $\Psi$  and  $\Delta$  are shown at 2.75 eV.

Moreover, surface solidification is not restricted to a specific alloy. So far it could be observed under comparable experimental conditions for three Ga-containing systems: GaBi, GaPb and GaTl, respectively. This is demonstrated for  $\Psi$  and  $\Delta$  versus temperature in figure 4. At high temperatures, when no solid film is present, the optical properties are dominated by liquid Ga which is doped with M ( $M = \text{Bi, Pb or Tl}$ ) to a small extent. After the jump in  $\Psi$  and  $\Delta$ , the surfaces of the alloys consist mainly of a solid film of M. The three alloys have various properties in common. First of all, the GaM phase diagrams are of the same type. They exhibit a broad liquid–liquid demixing regime terminated by an upper critical point and at the lower boundary by the monotectic reaction. The relevant phase line in our context here ranges from the Ga-rich monotectic point down to the Ga-rich eutectic. It separates the two phase region (solid M-rich phase and liquid Ga-rich phase) from the one phase region (liquid Ga-rich phase). In close vicinity to this phase line the surface freezing phenomenon is observed. Unfavorable for the formation of a solid M-rich phase on top of the Ga-rich liquid is in all three cases the higher density of solid M in comparison to liquid Ga. However, the existence of the Gibbs-adsorbed microscopic layer of M reduces the nucleation barrier for the formation of the solid film effectively [22].

In the case of GaPb and GaTl a serious problem is the exact location of the liquidus line between the monotectic and the eutectic point. In both cases it increases very steeply with the mole fraction of Pb or Tl, respectively. The eutectics as starting points of the liquidus curves are well known (GaPb:  $T_{\text{eut}} = 29.70\text{ °C}$ ,  $x_{\text{Pb}} = 0.0006$ ; GaTl:  $T_{\text{eut}} = 29.70\text{ °C}$ ,  $x_{\text{Tl}} = 0.0006$ ) but the compositions of the monotectic points (GaPb:  $T_{\text{mono}} = 313\text{ °C}$ ,  $x_{\text{Pb}} = 0.024$ ; GaTl:  $T_{\text{mono}} = 287\text{ °C}$ ,  $x_{\text{Tl}} = 0.018$ ) [10] are uncertain up to an amount of 30% [28]. This leads for both alloys to an uncertainty of the temperature of the phase line at  $x_{\text{M}} = 0.01$  within an interval of 30 K and at  $x_{\text{M}} = 0.001$  within 5 K. Therefore, an important question is how one can distinguish between the surface phase transition and the bulk phase transition along the liquidus line. The situation is clearer in the case of GaBi. Outside the error bar for the locus of the liquidus phase line the surface freezing line was detected a few kelvins above the liquidus [11]. Employing SHG this was shown convincingly for the eutectic  $x_{\text{Bi}} = 0.0022$ : a solid film appears on top of the liquid alloy at  $42\text{ °C}$ , well above the eutectic temperature of  $29.48\text{ °C}$  [29]. The melting of the film at  $49\text{ °C}$  is connected with a pronounced hysteresis classifying this transition as of first order. The hysteresis was observed in all cases when the cooling of the sample was stopped immediately after the formation of the film and the crossing of the liquidus line was avoided. In contrast to this the film melted below its formation temperature when the



**Figure 5.** Different patterns of melting behaviour of the film in a GaPb alloy, dependent on the target temperature  $T_{\min}$  approached on cooling ( $x_{\text{Pb}} = 0.0056$ ). Upper panel: the solid film exhibits a hysteresis and melts several K above  $T_{\text{SF}}$  if  $T_{\min} > T_{\text{SF}} - 6$  K. Lower panel: the solid film melts several K below  $T_{\text{SF}}$  if  $T_{\min} < T_{\text{SF}} - 6$  K. Scattering of data points is due to mechanical disturbances of the liquid surface.

sample was cooled below the liquidus line and bulk material could crystallize at the film [11]. Taking these experimental observations in the case of GaBi as an indicator for the separation of the surface freezing line on the one hand and the liquidus line on the other we may proceed to discuss figure 5. It shows two cooling/heating cycles of GaPb with  $x_{\text{Pb}} = 0.0056$ . The top panel shows the melting of the film at 192.5 °C when the preceding cooling of the sample was stopped immediately after the formation of the film at 188 °C. The contrary behaviour can be seen in the lower panel. The film was cooled to  $T_{\min}$  significantly below its solidification temperature  $T_{\text{SF}}$ , presumably below the liquidus line whose exact location is not known. In this case, i.e. when  $T_{\text{SF}} - T_{\min}$  is greater than approximately 6 K, the melting of the solid surface sets in significantly below  $T_{\text{SF}}$ , presumably at the liquidus temperature. This was reproducible for various runs of the same sample as well as for different samples with different compositions. In analogy to the results of GaBi we may arrive at the following conclusions: on cooling of a GaPb (or GaTl) sample a surface freezing transition precedes the bulk phase transition (solubility boundary of Pb in the Ga-rich liquid). Both phase lines are separated by only a few kelvins. Taking into account the pronounced and very reproducible changes at the surface freezing transition, this may serve to improve the determination of the liquidus line.

#### 4. Conclusions

The surface freezing characteristics of Ga-based alloys, the GaBi, GaPb and GaTl systems, have been investigated in detail by ellipsometry. They have the following important features in common: in the bulk phase they exhibit a liquid–liquid miscibility gap and at the liquid/vapour interface they are characterized by complete wetting transitions at liquid–liquid coexistence—the latter has been shown for GaBi and GaPb. In all these systems a surface freezing transition is manifested by a marked drop of the ellipsometric angles at temperatures above the liquidus, i.e. at conditions inside the homogenous liquid phase. The transition temperature  $T_{\text{SF}}$  is nearly



independent of the cooling rate and temperature difference of  $\pm 10$  K across the interface. Surface freezing and melting exhibit a clear hysteresis behaviour which strongly indicates that the transition is of first order. The surface freezing films are rich in the M component (M: Bi, Pb or Tl), which is concluded from the ellipsometric spectra. This is in quantitative agreement with surface analytical XPS measurements. However, the film thicknesses determined by both these methods are still controversial: the ellipsometric film thickness of GaPb is greater or equal 400 Å, whereas that from XPS is approximately 20 Å. Both are clearly higher than the value of approximately one monolayer derived from x-ray scattering data [9]. It may be noted that the sample geometries in all these experiments are different. So, further investigations are necessary to solve the thickness discrepancy. In this context the long term stability of the surface freezing films is of particular interest. By ellipsometry a long term drift on a timescale of hours and days has been observed. Furthermore, it seems that the film kinetics strongly depend on the target temperature  $T_{\min}$  to which the sample is cooled below  $T_{\text{SF}}$ . Further studies of these points are needed.

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