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Structural change with the resistance drift phenomenon in amorphous GeTe phase change materials' thin films

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Abstract

Ageing of the amorphous phase of chalcogenide phase change materials is characterized by a large increase of their resistivity with time. This phenomenon, known as resistance drift and commonly attributed to structural relaxation, the nature of which remains unknown, has until now hindered the development of ultra-high multilevel storage devices. The origin of the resistance drift of amorphous GeTe thin films is studied here by resistivity measurements and grazing incidence x-ray absorption spectroscopy (GIXAS). The local order around Ge atoms is investigated at the Ge K-edge on a-GeTe samples previously set at different resistance drift levels by thermal annealing. In all samples, Ge–Ge and Ge–Te bonds coexist. This study demonstrates that the drift phenomenon is concomitant with structural changes linked to Ge–Ge homopolar bonds.

Keywords: chalcogenide, drift, XAS, phase change, GeTe

(Some figures may appear in colour only in the online journal)

1. Introduction

Chalcogenide phase change materials (PCMs) such as GeTe and Ge₂Sb₂Te₅ (GST 225) exhibit the ability to switch reversibly between crystalline (c-) and amorphous (a-) phases with different optical and electrical properties [1]. They have been used for a long time for optical recording in DVD-RAM. Due to the large difference in the electrical properties of the (c-) and (a-) phases, PCMs are also giving rise to an intense research effort towards the development of phase change random access memories (PCRAM), which are expected to challenge

DRAM or current FLASH memory technologies [2]. The time evolution of the resistance of the PCM amorphous phase (resistance drift) has a strong impact on the retention of the information in multi-level cells where several bits are stored corresponding to different resistance values [3]. The increase by many orders of magnitude of the PCM cell resistance with material ageing can lead to memory failure and hindered up to now the development of ultra-high multilevel storage devices. Thus, reducing the drift is one of the technological challenges in the development of such resistive memory systems, which are on the threshold of mass production for embedded applications. In particular, high temperature embedded applications require the use of innovative alloy compositions with a higher crystallization temperature T_x than GST 225. This is

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obtained either by doping with C and N or by increasing the Ge fraction, in the latter case with the drawback of a larger resistance drift [4].

The resistance drift is observed after deposition of an amorphous thin film or after the RESET of a memory cell. At a given temperature, the resistance of the amorphous phase increases with time and obeys a power-law which can be quantified by the drift coefficient ν [3]. Different values of ν are observed as a function of the PCM alloy composition (Ge/Sb/Te ratio or dopant incorporation). For example $\nu \sim 0.1$ for GST 225 [5]. Publications in the current literature aiming to understand the resistance drift mechanism agree on the fact that the drift is due to some kind of relaxation of the amorphous structure. However, they propose very different, and sometimes opposing, physical mechanisms, such as increase [6] or decrease [5, 7] of disorder, increase [8] or decrease [9] of the defect density of states, drift impacted [10] or not impacted [11] by stress. This confused situation arises from the lack of structural studies of the a-phase as a function of ageing. Such a study is presented here in the case of a-GeTe. This binary alloy is the end-point of the well-studied pseudo-binary line to which GST 225 belongs [12]. Its ν value is around 0.125 ([5] and references therein). It is a good candidate for applications since its crystallization temperature is higher than that of GST 225. It has been the subject of numerous *ab initio* molecular dynamics simulations [13–18]. As a result, the local environment of Ge in a-GeTe is a mix of tetrahedrally bound Ge and Ge in a defective octahedral environment with bond angles close to 90° . Thus, the average coordination of Ge atoms is close to 4. Ge–Ge bonds are found in the tetrahedra. In contrast, in distorted octahedral sites, Ge is mainly surrounded by Te. Note that tetrahedral Ge sites are not present in the rhombohedral crystalline GeTe phase, which is composed only of distorted octahedra in which Ge is bound to Te, with three short and three long Ge–Te bonds. In the literature the existence of a tetrahedral environment in a-GeTe has been correlated with the presence of a large amount of Ge–Ge homopolar bonds [16–20]. The presence of Ge–Ge bonds and tetrahedrally coordinated Ge atoms has also been deduced from simulations in the case of GST [21–23]. Moreover it has recently been proposed in [18] that homopolar bonds directly contribute to the local stability of the tetrahedra in a-GeTe. It is suspected that homopolar Ge–Ge bonds modify the a-GeTe Density Of States (DOS) and band structure [17–19]. The relaxation of the amorphous state and the resistance drift could be linked to the removal of tetrahedrally coordinated Ge sites and Ge–Ge bonds, leading to an increase in the band gap and to the removal of localized defects in the gap [19, 20]. A different mechanism is invoked in [17], which proposes that the formation of Ge–Ge bonds generates free electrons that contribute to the material conductivity. In this model, the resistance drift in a-GeTe is ascribed to the breaking of Ge–Ge bonds, inducing partial recombination of free electrons and hence a decrease in the concentration of free charge carriers. Other models have been proposed since many different types of structural defects [7] (e.g. dangling bonds, distorted bonds, vacancies ...) can also introduce

localized states in the band gap and evolve with ageing. Thus, no clear picture exists up to now.

In this paper, direct experimental evidence of structural changes with resistance drift is presented. The local structure around Ge atoms is investigated by grazing incidence x-ray absorption spectroscopy (GIXAS) at the Ge K-edge on amorphous GeTe thin film samples. The a-GeTe films were set at different resistance drift levels by thermal annealing prior to the XAS experiment. The drift level was controlled by resistivity measurements. In all samples, Ge–Ge and Ge–Te bonds coexist. A clear change of the homopolar Ge–Ge bonds with drift is observed. The number of Ge–Ge bonds increases as the resistance increases, which is contrary to current theoretical predictions in the literature [17, 19, 20].

2. Methodology

The a-GeTe layer was obtained by magnetron sputtering of a pure stoichiometric target ($\text{Ge}_{50}\text{Te}_{50}$) in a CLN200 industrial cluster tool from Oerlikon. To allow resistivity measurements, the 100 nm thick a-GeTe film was deposited on an insulating layer consisting of a 500 nm thick thermal silicon oxide on top of a 200 mm diameter Si substrate. The thickness and density homogeneity of the deposited layer were controlled by x-Ray Reflectivity. The composition of the film was measured by Rutherford Back Scattering and Wavelength Dispersive x-Ray Fluorescence. The composition obtained, $\text{Ge}_{52.4 \pm 0.6}\text{Te}_{47.6 \pm 0.6}$, is close to that of the target, with only a small excess of Ge, as is always found in a-GeTe films deposited by magnetron sputtering, despite the use of a stoichiometric target [24]. The density of $5.3 \pm 0.3 \text{ g cm}^{-3}$, obtained from these characterizations, is close to the usual value [25]. Finally, the a-GeTe film was capped *in situ* directly in the deposition tool with a 10 nm-thick SiN layer in order to avoid surface reactions or oxidation due to exposure to the atmosphere. In fact, such surface reactions are expected to promote Te–O surface desorption during thermal annealing. Furthermore, the presence of surface Ge–O bonds resulting from oxide formation can significantly affect the XAS analysis.

Four-point probe resistivity measurements were carried out as a function of time while heating the a-GeTe film under N_2 atmosphere at fixed temperature. First of all, in figure 1(a) the results obtained for an isothermal resistivity measurement of a sample heated at 50°C for 72 h are shown in order to quantify the resistance drift phenomenon. By fitting the experimental data to the commonly used power-law $\rho(t) = \rho_0(t + t_0)^\nu$, where ρ is the resistivity and ρ_0 the initial resistivity, a drift exponent $\nu \sim 0.145 \pm 0.02$ at 50°C (323 K) is deduced. This ν value is in good agreement with the results of [5]. In a second step, 3 distinct a-GeTe samples named D1, D2 and D3 were set at different resistance drift levels by thermal annealing at a constant temperature (50°C under the crystallization temperature) for respectively 1, 15 and 30 min. The resulting resistivity values at 300 K are shown in figure 1(b). During the annealing, the optical reflectivity and resistivity of the samples were constantly monitored to ensure that no crystallization occurred. The sample denoted D0 is an as-deposited

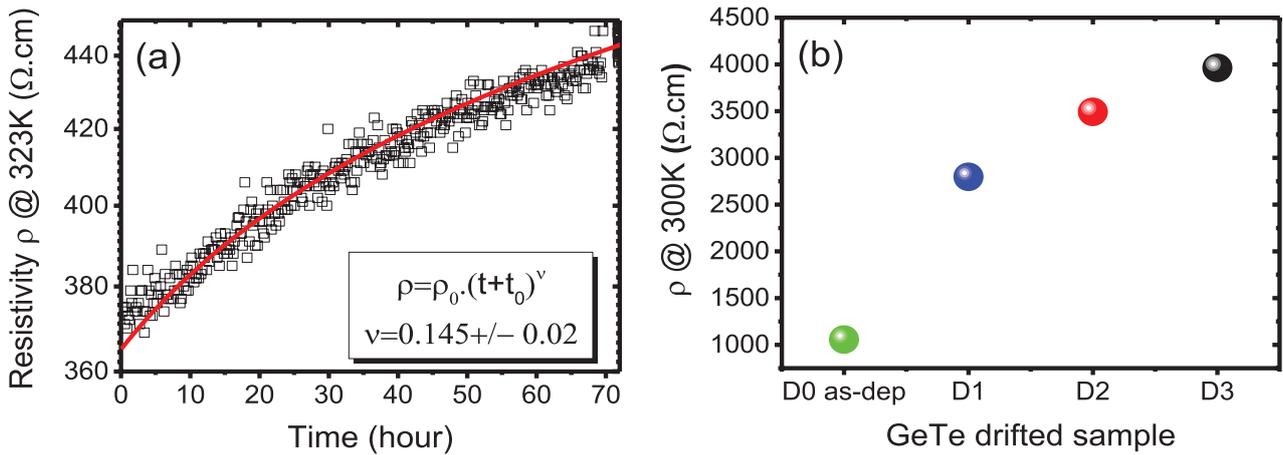


Figure 1. (a) Four-point probe resistivity measured at 323 K (50 °C) as a function of time on the 100 nm thick a-GeTe film showing the time dependent increase of the resistivity ρ (drift). The fit of the power-law relation $\rho(t) = \rho_0(t + t_0)^\nu$ (continuous line) to the experimental data (squares) yields the drift coefficient $\nu \sim 0.145 \pm 0.02$. (b) Resistivity ρ measured at 300 K on the as-deposited a-GeTe sample (D0) and on three a-GeTe samples (D1, D2 and D3) set at different ageing and resistance drift states, after different thermal annealing.

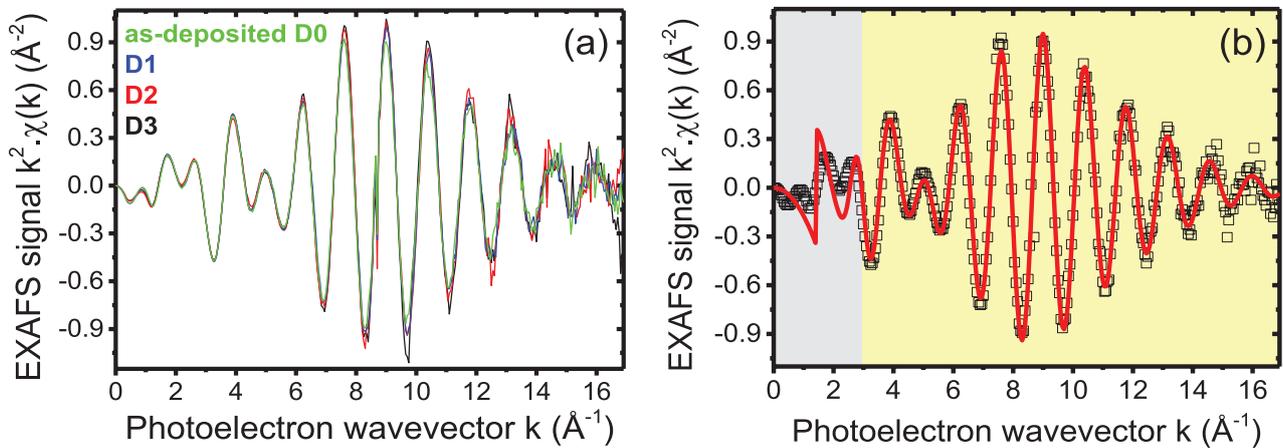


Figure 2. (a) EXAFS spectra of a-GeTe samples in different resistance states according to figure 1(b). (b) EXAFS spectrum (squares) with the best fit curve (continuous line) for the a-GeTe sample in the as-deposited D0 resistance state.

a-GeTe film used as a reference sample. Its drift level is due to ageing at room temperature for less than one month. The three thermally aged samples (D1, D2 and D3) and the as-deposited D0 were then analyzed by GIXAS to look for any structural change associated with the resistance drift phenomenon.

XAS measurements at the Ge–K edge ($E = 11103$ eV) were carried out at room temperature at the LISA-BM08 beamline at the ESRF [26]. The x-ray optics consisted of a sagittally focused Si(311) monochromator crystal and two Pd-coated mirrors for vertical focusing and harmonic rejection with a cut-off energy of 18 keV. The grazing incidence mode was used with an incidence angle of 1° and data collection was carried out with fluorescence mode using a 12 element energy resolving high purity Ge detector.

3. Results and discussion

The EXAFS (extended x-ray absorption fine structure) of a-GeTe samples D0 (as-deposited), D1, D2 and D3 are shown in figure 2. Qualitatively, the spectra look similar with however a progressive increase of the oscillation amplitude as the

resistance increases from D0 to D3. The Fourier transforms (FT) of the spectra displayed in figure 2 are plotted in figure 3. A remarkable point is that no peak is visible at low R values (around 1.3 \AA), where Ge–O bonds would contribute to the FT, which means that no oxide phase can be detected in the studied samples. Such a result is particularly noteworthy since PCM films are known to be easily and quickly oxidized in the presence of oxygen. This confirms the absence of oxidation during the preparation process and the ability of the *in situ* capping to prevent subsequent oxidation. It guarantees that the structural changes discussed hereafter are not due to changes in an oxide layer. The FT spectra exhibit a main peak centered around 2.3 \AA which becomes increasingly intense as the resistance drift level increases. The experimental data were modeled with 2 coordination shells Ge–Ge and Ge–Te. It is worth noticing that the backscattering amplitudes of Ge and Te exhibit considerable differences at low k values (namely for $k < 6 \text{ \AA}^{-1}$) [27], which makes easier the distinction of their contributions to the total spectrum. Self-absorption effects, estimated to affect about 20% of the signal amplitude, were accounted for using the Booth method implemented in

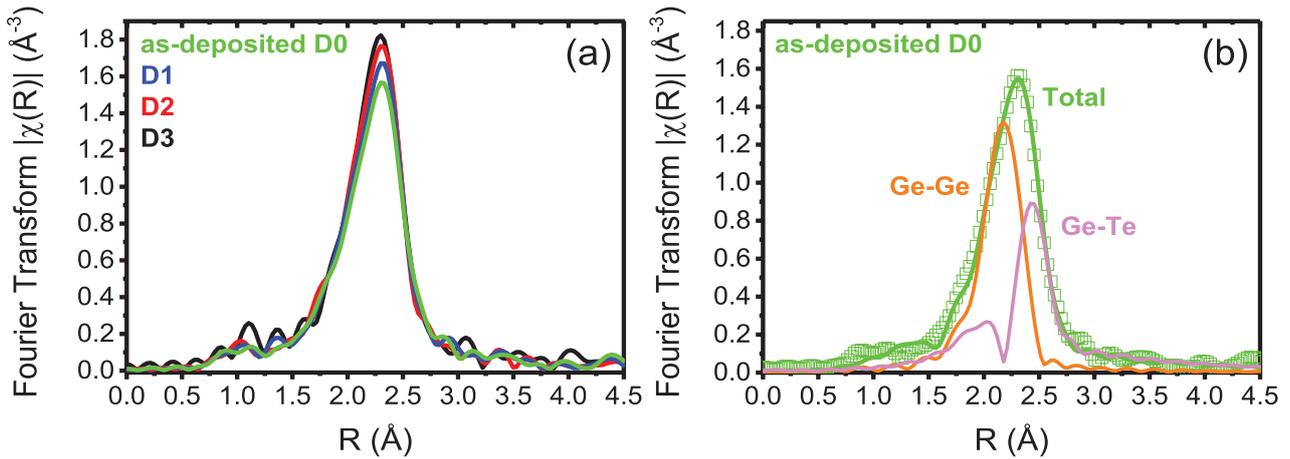


Figure 3. (a) Fourier transforms of the k^2 weighted spectra of figure 2(a) from a-GeTe samples in different resistance states. The Fourier transforms were carried out in the k interval $[3-16.9] \text{ \AA}^{-1}$. (b) Fourier transform (squares) with the best fit curve (continuous line) of the EXAFS spectrum of figure 2(b) from the a-GeTe sample in the as-deposited D0 resistance state. The fit of the FT was performed in R space in the R interval $[1.1-2.9] \text{ \AA}$. The partial contribution of Ge-Ge and Ge-Te bonds to the total calculated FT are also plotted in figure 3(b). The splitting of the Ge-Te bond contribution is due to the Te backscattering amplitude (Ramsauer-Townsend resonance).

Table 1. Quantitative results of the XAS data analysis. The data were modelled with a two shell model Ge-Ge and Ge-Te. The global amplitude reduction factor S_0^2 , derived from the spectrum of pure Ge collected in transmission mode, was $S_0^2 = 0.90(5)$. The same value was used for all the samples. Debye Waller factors were initially fitted but it was found that all the values superimposed within the error bars. Thus, they were fixed at their average values $\sigma_{\text{Ge-Te}}^2 = 0.0035 \text{ \AA}^2$ and $\sigma_{\text{Ge-Ge}}^2 = 0.0056 \text{ \AA}^2$ for the final fit, which led to reduced error bars on the coordination numbers. The use of higher cumulants of the pair distribution function was attempted but did not lead to significant improvements. The values indicated in brackets are the errors on the last digit estimated by the IFEFFIT code as the diagonal elements of the covariance matrix divided by the square root of the reduced χ^2 .

a-GeTe sample	$N_{\text{Ge-Ge}}$	$R_{\text{Ge-Ge}} (\text{\AA})$	$N_{\text{Ge-Te}}$	$R_{\text{Ge-Te}} (\text{\AA})$
as-dep D0	1.65(7)	2.473(5)	1.38(7)	2.628(5)
D1	1.73(7)	2.471(4)	1.46(7)	2.62(1)
D2	1.86(7)	2.471(5)	1.42(7)	2.618(5)
D3	1.89(7)	2.473(5)	1.47(7)	2.62(5)

the ATHENA code [28]. The results of the quantitative data analysis are listed in table 1. The mean Ge-Ge distance $R_{\text{Ge-Ge}}$ is $\sim 2.47 \text{ \AA}$ while the mean Ge-Te distance is larger ($R_{\text{Ge-Te}} \sim 2.62 \text{ \AA}$). They are in agreement with previous reports [29, 30]. These distances are the same for the different samples. $N_{\text{Ge-Ge}}$, the Ge-Ge coordination number, increases with ageing and drift of the a-GeTe film, as is clearly shown in figure 4. $N_{\text{Ge-Te}}$, the Ge-Te coordination number, fluctuates within the error bars and no clear trend can be established. The total coordination of Ge varies from 3.0 to 3.4 from D0 to D3. The XANES spectra (not shown here) display no significant change or trend with ageing and drift.

As shown above, the ageing of the a-GeTe film is accompanied by a clear change of the amorphous structure with an increase of the number of Ge-Ge bonds. According to the literature, the number of Ge-Ge bonds is directly related to the number of tetrahedral units. Hence the present experiment would suggest that the number of tetrahedra increases with drift and ageing of a-GeTe. Note that this result cannot

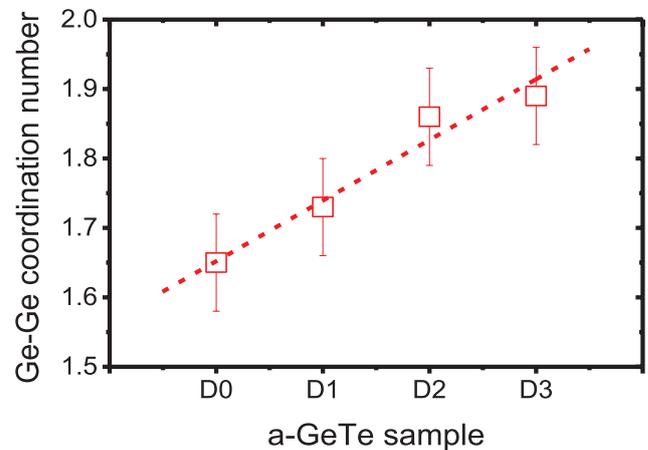


Figure 4. Plot of the Ge-Ge coordination number deduced from fits of the EXAFS experimental data as a function of the resistance drift level of a-GeTe films. The dashed line is a guide for the eye.

be compared with structure simulations of a-GeTe, since the large time scales involved in the ageing phenomenon in the experiments are not accessible to *ab initio* simulations. Besides, simulations of the structural relaxation in a-GeTe [19, 20] are performed from a melt-quenched amorphous state, whereas we observed the structural changes of an as-deposited a-GeTe. In this context, it is interesting to note that the change of the FT with ageing shown in figure 3 is reminiscent of that observed in [31] from the melt-quenched state to the as-deposited state of GST 225. In the latter case, the observed increase of the Ge-Ge bond contribution to the FT of the EXAFS at the Ge K-edge is corroborated by *ab initio* simulations that predict a larger proportion of tetrahedral Ge and of Ge-Ge bonds in the as-deposited state than in the melt-quenched state [22]. The only previous experimental observation of a structural change with ageing is the XANES study of [32], where a small shift of the Ge-L_{III} edge with ageing has been reported in GST 225 and ascribed to a gradual reduction of the number of tetrahedrally coordinated Ge. Nevertheless, in this study [32], the link with the resistance is not clear since

this continuous change of the XANES spectrum with ageing is accompanied by a resistance increase followed by a resistance decrease.

Homopolar Ge–Ge bonds might introduce defect states in the band gap [19] or free electrons [17]. If so, an increase in their number would be expected to decrease the resistance. The trend found here, where the number of Ge–Ge bonds increases as the resistance increases, is in the opposite direction. It must be emphasized that many other structural defects [7] (e.g. dangling bonds, distorted bonds, vacancies ...) can introduce localized states in the band gap and hence contribute to the conductivity of the material. The drift phenomenon certainly involves several contributions. In particular, the reduction of the number of dangling bonds with annealing and ageing [7] could explain the observed trend in the EXAFS spectra and the increase in resistance. In addition to changes in defect states, an increase of the band gap, and hence of the resistance, could be related to an increase of the Peierls distortion. In the EXAFS spectra such an effect would be detected through a shortening of the Ge–Te distance but, within accuracy of the experiment, this is not the case in the present study. Finally, it should be mentioned that the correlation between the increase in Ge–Ge coordination number and resistance drift could also be attributed to the appearance of a-Ge sub-nuclei in the amorphous phase of GeTe due to the slight Ge-excess present in a-GeTe films deposited by sputtering. This phenomenon has already been proposed in [33] in the case of GST. Indeed, Ge–Ge bonds having larger energy difference between bonding and anti-bonding states than Ge–Te ones, the formation of sub-critical a-Ge nuclei with a larger band gap in the a-GeTe phase should lead to an increased band gap for the overall amorphous material and an increase of its resistivity with time and ageing. Moreover, such phenomenon, which should be accompanied by a stress relaxation, would be at the origin of an increase of the band gap and hence increase in resistivity of the a-GeTe film with drift [33]. Such last hypothesis will thus need further investigations in order to be definitively concluded.

4. Summary

In conclusion, analysis of the EXAFS at the Ge K-edge on a-GeTe samples set at different resistance values by thermal annealing, demonstrates that, whatever the drift level, both Ge–Ge and Ge–Te bonds constitute the local environment of Ge. The preparation conditions that ensure absence of oxidation of the GeTe film allow us to detect clearly a change in the local Ge environment with ageing and drift of the amorphous film. The number of Ge–Ge homopolar bonds, and hence the fraction of tetrahedrally coordinated Ge, increases as the resistance increases. This effect could be related to a decrease of defect states in the band gap, induced by the structural changes, leading to a progressive increase in resistivity of the amorphous semiconductor. In any case, the impact of the observed structural changes on the electronic structure of the amorphous phase will have to be taken into account in models. These results are of great importance in designing

phase change materials that exhibit very low resistance drift in the amorphous phase.

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