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Electrical properties of amorphous chalcogenide/silicon heterojunctions modified by ion implantation

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ABSTRACT

Doping of amorphous chalcogenide films of rather dissimilar bonding type and resistivity, namely, Ga-La-S, GeTe, and Ge-Sb-Te by means of ion implantation of bismuth is considered. To characterize defects induced by ion-beam implantation space-charge-limited conduction and capacitance-voltage characteristics of amorphous chalcogenide/silicon heterojunctions are investigated. It is shown that ion implantation introduces substantial defect densities in the films and their interfaces with silicon. This comes along with a gradual decrease in the resistivity and the thermopower coefficient. It is shown that conductivity in GeTe and Ge-Sb-Te films is consistent with the two-type carrier conduction model. It is anticipated that ion implantation renders electrons to become less localized than holes leading to electron conductivity in certain cases as, for example, in GeTe.

1. INTRODUCTION

Majority of amorphous chalcogenides are layered materials known to comprise weak van der Waals bonding of the layered units. As in the case of many organic counterparts, this feature of amorphous chalcogeindes opens possibility to adjust their electronic properties *via* the local structural re-arrangement. However, doping of these materials has been proved to be hindered by the structural flexibility of the amorphous network, which allows for the formation of energetically favourable coordination defects, designated as valence-alternation states [1]. Although the effects of impurities on the electronic properties of chalcogen-based amorphous semiconductors have been considered controversial, alloying with lithium, bismuth and lead in melted glasses has been shown to modify the conductivity [2, 3]. With respect to doping, only Bi and Pb have been found to reverse the carrier type, from p- to n-type, in amorphous chalcogenide semiconductors by means of equilibrium doping. The origin of the n-type conductivity in bismuth-modified bulk chalcogenide glasses has been explained to originate from the high polarizability of bismuth, which favours the formation of partially ionic Bi-chalcogen bonds [4]. From theoretical consideration, percolation-controlled conduction by n-type nano-inclusions in heterogeneous amorphous chalcogenides has been proposed [5, 6]. It has been suggested that the 8-N rule, formulated by Mott, does not satisfactorily describe impurity states in the band gap of amorphous chalcogenides whose alloy compositions are substantially heterogeneous. In this case the electrical properties of the amorphous matrix will be determined by the atomic structure of the nano-nonuniformities, which can accommodate an increased atomic coordination around an introduced dopant. Hence, an impurity atom within such a nano-inclusion behaves as it does in crystalline semiconductors [6].

Doping of amorphous chalcogenides can be implemented using different approaches and technological methods - thermal evaporation, magnetron sputtering, or doping in the melt. In the latter case, a slow liquid quench enables a balanced equilibrium with recrystallization acting as a balancing force, thus implying high doping concentrations are required to shift a melted alloy to a non-homogeneous state of a sufficiently perturbed local coordination around an introduced dopant. Regardless of the doping method, transition from p- to n-type conductivity in chalcogenide glasses doped with Bi has been predicted to arise from n-type defects formed in the glassy network [7]. It has been established

that impurity conductivity with an activation energy E_A, smaller than half of the band gap, readily arises when introduced dopant atoms cannot equilibrate with an amorphous matrix. Hence, non-equilibrium growth or doping techniques are thought to be beneficial in introducing alloy disorder. Here, we address the impact of ion implantation, in particular of bismuth, on the electrical properties of Ge-Sb-Te and GeTe amorphous semiconductors of rather dissimilar bonding type. The interchain bonding of Ge-Sb-Te and GeTe has been found to differ. Stronger and more elastic Te-Ge-Te bonds in Ge-Sb-Te may account for dissimilar crystallization behaviour of GeTe and Ge-Sb-Te [8].

Another aspect, which may be of interest in respect to amorphous chalcogenide films is related to device implementation and formation of interfaces of chalcogenide semiconductors with crystalline semiconductors such as Si, Ge, and III-V compounds. It is suggested that *at the interface* charge trapping may violate charge neutrality of positively and negatively charged *D*-centres mutually compensating each other in the bulk of amorphous chalcogenides. Thus, the resulted trapped *interfacial charge* could modulate the band bending and serve to effectively passivate semiconductor surfaces. It is expected that modifying the chalcogenide glasses one also changes electronic properties of the interfaces, however, this problem has rarely been addressed so far.

Here we show, based on measurements of thermopower, conductivity, and capacitive responses that defects arising as a result of ion implantation effectively dope Ge-Sb-Te and GeTe films.

2. EXPERIMENTAL

We have studied 100 nm thick Ge-Sb-Te and GeTe films prepared by rf sputtering, either on silicon to form heterojunction devices, or on fused silica substrates to probe the conductivity by means of thermopower measurements. Ion implantation of Bi was done using a Danfysik ion implanter with doses in the range of 1×10^{14}-1×10^{16} cm^{-2} at energy of 190 keV. The samples for the current-voltage (*IV*) and capacitance-voltage (*CV*) measurements were completed by depositing gold electrodes of area $(1.75$–$2.25) \times 10^{-2}$ cm^2. The *IV* and *CV* traces were recorded using an Agilent B2902A source-measurement unit and an HP4275A LCR meter in the temperature range from 77K to 300K on samples mounted in an Oxford OptistatDN cryostat which was connected to a temperature controller. The total interface trap density N_{it} (integrated across the Si band gap) was determined from the absolute difference of the flat-band voltage V_{fb} inferred from high-frequency *CV* curves taken on p- and n-type Si MOS-capacitors at 77 K, as described elsewhere [9]. The dopant concentrations in the n-type and p-type silicon substrates determined after the gold electrodes and the chalcogenide films were removed by concentrated hydrofluoric acid and nitric acid were equal to $2.0 \pm 0.1 \times 10^{15}$ cm^{-3} and 5×10^{15} cm^{-3}, respectively. The relative permittivity of the Ge-Sb-Te and Ga-La-S films required for the N_{it} estimation and analysis of space-charge limited conduction in the amorphous chalcogenide films was calculated by using $\varepsilon = n^2 \text{-} k^2$, where n and k are, respectively, the refractive index and extinction coefficient determined from spectroscopic ellipsometry data. The latter were obtained using a Sopra GES-5 instrument. The measured spectra were fitted with the help of the Tauc-Lorentz dispersion model. For the amorphous as-deposited Ge-Sb-Te films, the n and k values are taken from the data presented in Fig 5 of Ref. 10. The optical absorption spectra were obtained using a Varian Cary 5000 UV-vis-near IR spectrophotometer. For the thermopower measurements, the films were deposited on fused silica substrates. An air gap between a copper block and a resistively heated suspended thermal contact provided the temperature gradient between the electrodes spaced 1 cm apart. The samples were shielded from external voltages and isolated from ground.

Compositional uniformity and stoichiometry of selected as-deposited and implanted films was determined by means of Rutherford backscattering (RBS) in normal incidence using 2MV Tandetron accelerator [11]. The elemental distribution in as-deposited films is found to be uniform. Substantial oxygen content in GeTe films is evidenced by the mole ratios of O/Ge equal 0.8. Upon incorporation of Bi, the GeTe films show substantial loss of Te atoms. The Bi implantation in GeTe is accompanied with oxidation of GeTe.

3. RESULTS AND DISCUSSION

Fig. 1 exemplifies temperature dependences of the resistivity and the thermopower for Ge-Sb-Te and GeTe films implanted with bismuth. The temperature dependence of the resistivity for Ge-Sb-Te, Fig. 1(a), shows two distinctly different values of the activation energy, E_A, below and above 360K-370K for the case of the as-deposited samples (□) and the samples implanted at a relatively low dose of 5×10^{14} cm^{-2} (○).The activation energy determined at temperatures below 370K is seen to be insensitive to the implantation dose and falls within the range of 0.35 ± 0.05 eV for as-deposited and the Bi-implanted samples. The temperature dependences of the resistivity for GeTe films are shown in Fig. 1(b). Compared to the Ge-Sb-Te case, only one activation energy of the conductivity is observed in the same temperature range. The experimental data points (◁,▷) are seen to level off at lower temperatures, indicating the

contribution of a hopping-conduction mechanism. The E_A values of 0.7-0.8 eV, characteristic of the unimplanted films, sharply decrease to 0.2-0.25 eV after implantation of Bi at doses of 5×10^{15} cm^{-2} and 2×10^{16} cm^{-2}, [cf. ($\otimes$, $\star$) in Fig.1 (b)]. The thermopower coefficient S as a function of the Bi dose is shown in Fig. 1(c, d). Qualitatively similar dependences of S for the Ge-Sb-Te and GeTe films suggest that the same processes are responsible for the observed modification of the conductivity and the change in the carrier transport mechanism. However, the resistivity of GeTe as a function of the Bi-implantation dose decreases monotonically with the implantation dose, whereas for the Ge-Sb-Te films, a non-monotonic dependence of the resistivity as a function of the implantation dose is observed, with a minimum value around 1×10^{15} cm^{-2}, [cf. ($\triangle$) in Fig. 1(a)]. In the case of GeTe, a negative sign for the majority carriers follows from the thermopower data for the film implanted with Bi at a dose of 2×10^{16} cm^{-2}, as shown by ($\star$) in Fig.1 (d). In the case of Ge-Sb-Te, the implantation dose of 2×10^{16} cm^{-2} causes almost a complete removal of the films due to sputtering by the impinging ions. The increase in the resistivity of the Ge-Sb-Te films is thought to be related to this partial film removal at implantation doses of Bi higher than 1×10^{15} cm^{-5} and/or chemical-bond rearrangements. Upon Bi implantation, σ_0, Fig. 2, defined as $\sigma_0 = N(T) \cdot q \cdot \mu(T)$ *decreases* with the implanted dose. Such low values suggest either lower mobility or considerably smaller density of states. For conduction supported by small polarons thermopower is determined as the average of number of hops along the conduction path [12].
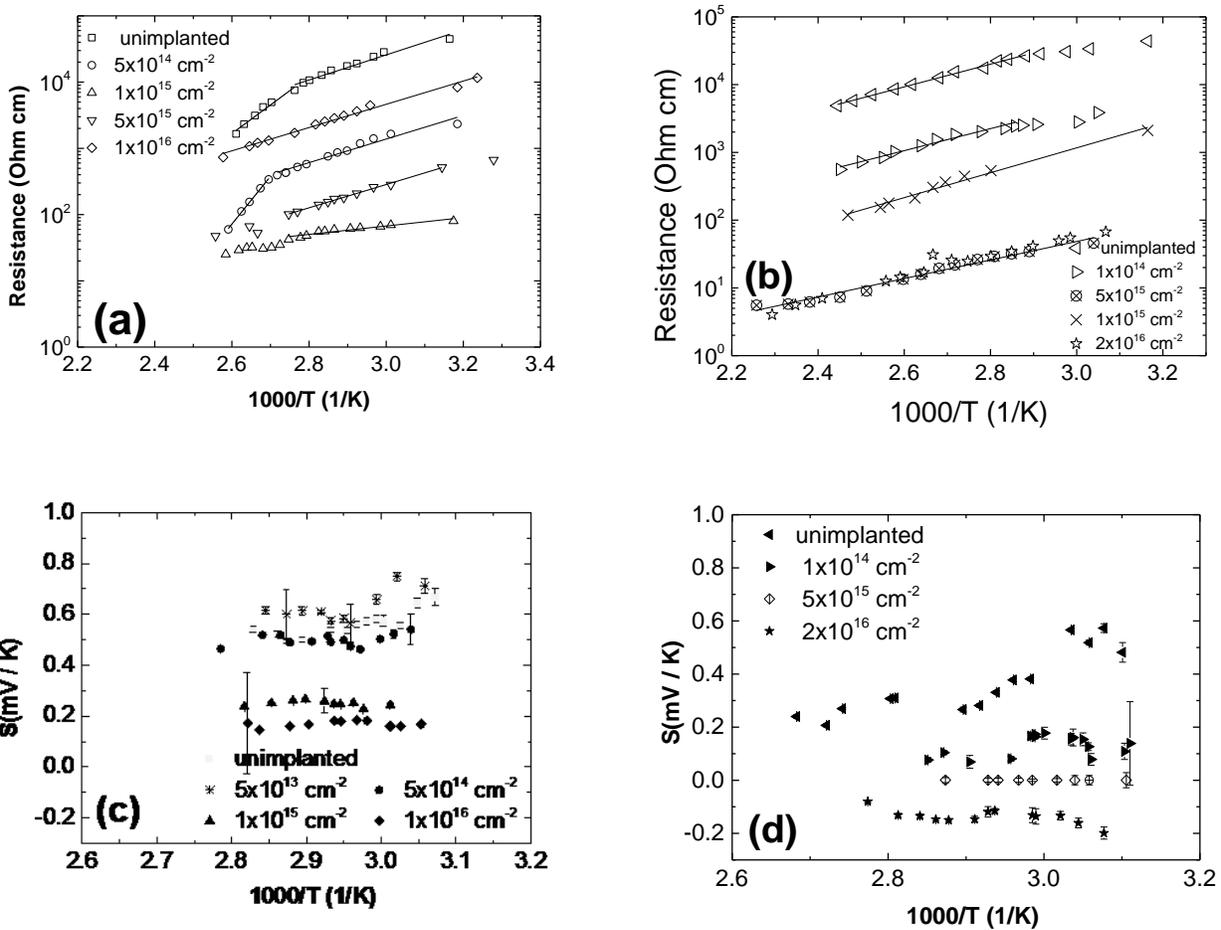

Figure 1. The resistivity ρ for Ge-Sb-Te and GeTe films is represented using open symbols on panel (a) and panel (b), respectively; the slope of the Seebeck coefficient S is shown by filled symbols on panel (c) and on panel (d) for Ge-Sb-Te and GeTe, respectively. Implantation doses of Bi are denoted as the following: 5×10^{13} cm^{-2} ($\ast$), 5×10^{14} cm^{-2} ($\bullet$,$\circ$), 1×10^{15} cm^{-2} ($\blacktriangle$,$\triangle$), 5×10^{15} cm^{-2} ($\blacktriangledown$), 1×10^{16} cm^{-2} ($\blacklozenge$,$\lozenge$) for Ge-Sb-Te; 1×10^{14} cm^{-2} ($\blacktriangleright$,$\triangleright$), 1×10^{15} cm^{-2} ($\times$), 5×10^{15} cm^{-2} ($\otimes$,$\oplus$), 2×10^{16} cm^{-2} ($\star$,$\ast$) for GeTe. Squares ($\square$,$\blacksquare$) and left-turned triangles ($\triangleleft$,$\blacktriangleleft$) correspond to as-deposited Ge-Sb-Te and GeTe samples, respectively.
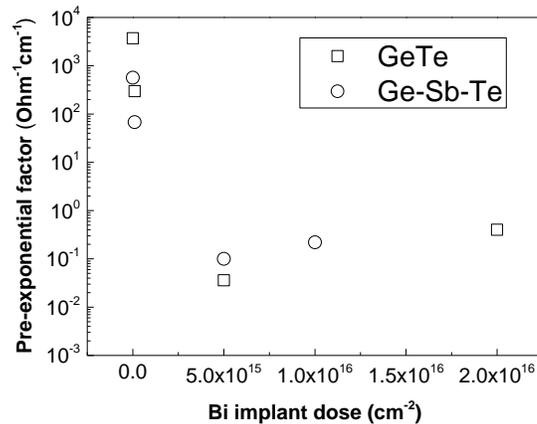
Figure 2. Pre-exponential factor σ_0 for thermally activated conductivity.

In our case we did not observe A to be close to unity. The constant A is negative for all studied films, in accord with earlier observations on negative A values found for GeTe and Ge-Sb-Te compounds [13, 14]. It is plausible to explain charge carrier transport in the studied entities in terms of two type charge carrier conductivity. Ion implantation greatly affects mobility of self-trapped holes and electrons, possibly rendering self-trapped electrons to become more mobile than holes. Within the frame of the small polaron theory, no limitation on a particular phase composition, heterogeneity or phase separation of a material may exist, because the charge is transported by structural units comprising an amorphous matrix of a chalcogenide compound. Increase in conductivity can be explained as a better conductivity of existing structural units, or formation of new conductive paths as it has been previously discussed in the case of As-Te chalcogenide glasses [15]. It is likely, that ion implantation of bismuth enhances defect density and rigidity of amorphous network through formation of interfaces percolating through the chalcogenide films; interfacial bonding constraints could partially account for increased density of defects [16]. Than the electron conductivity is thought to be set by elastic stiffness threshold which is associated with interatomic interactions such as bond stretching and bond bending, with the weakest one being of the van der Waals type.

Figure 3 exemplifies the forward JV-characteristics for Ge-Sb-Te on a *log-log* scale. Space-charge-limited conduction (SCLC) is apparent, as follows from the steeper JV-curves and the temperature-induced voltage shift towards higher voltages as the temperature decreases [17]. The experimental data can be fitted by the expression $J \propto V^m$. Values of m > 2 evidence an exponential trap distribution, as expected for traps originating from surface defects and structural disorder [18]. Quantitative information about the traps can be obtained by extrapolating the JV-curves with voltage [19]. If the charge traps are distributed in energy, there will be a gradual filling with an increasing electric field at all temperatures until, at a certain critical voltage V_c, all traps will be filled. This critical voltage is independent of temperature and is given by $V_c = qN_t d^2/2\varepsilon\varepsilon_0$. The V_c and N_t data obtained by extrapolating the JV-curves and listed in Table 1 show that the increase in the trap density is directly related to the Bi-dose.

Figs. 4 show dispersion-free Mott-Schottky curves taken at 77K on the heterojunctions (HJs) formed on p- and n-type silicon. At 77K, the vast majority of the interface traps are below the Fermi level. This permits a correct determination of the flat-band voltage V_{fb} in the heterojunction devices. Typical JV-characteristics of p-n and p-p Ge-Sb-Te/Si(100) HJs at 300K and 77K are shown in the insets of Fig. 4. Electron injection from silicon occurs under positive bias on the chalcogenide, as exemplified by the forward-current characteristics observed for the p-n devices and the saturation behaviour for the p-p-devices. The rectification behaviour observed for the p-p HJs suggests that the bend bending determines the device characteristics. The inferred total interface trap density, N_{it}, is one order of magnitude higher in the implanted samples. None of the studied HJs show CV-traces typical for a metal-oxide-semiconductor structure due to relatively high carrier generation rate in chalcogenide films and low interface barriers for electrons and holes at the Si/chalcogenide interfaces, thus preventing formation of inversion and accumulation layers in silicon. The increase in the total trap density in the Ge-Sb-Te heterojunction devices is accompanied by a larger V_{fb} shift towards positive values for n-Si HJs suggesting presence of acceptor states in the Bi-implanted Ge-Sb-Te/Si interfaces. The V_{fb} shift does not stem from a parallel translation of CV-curves along the voltage axis, indicative of oxide charge build-up, but arises from a difference in the slope of the Mott-Schottky curves (not shown here). For higher implantation deses, the increase in the flat band voltage determined on n- and p-type shows asymmetry. This implies asymmetry in the

interface state energy distribution in respect to the silicon midgap unlike known symmetric two-peak pattern characteristic to the (+/0) and (0/-) transitions of the P_{b0} defect and equal density of acceptor and donor interface traps observed for the Si/SiO_2 interface [12]. The interface trap built-up is unlikely to stem from displacement damage in silicon, because at the implantation energy of 190 keV Bi peaks at 50 nm from the top surface of the film. It is not unreasonable to suggest that the as-deposited chalcogenide films contain strained bonds or/and weakly bonded hydrogen known to serve as precursor sites for interface trap generation [20].
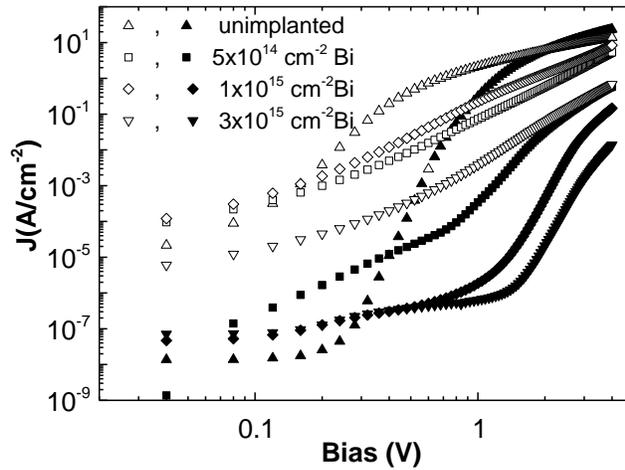

Figure 3. Forward current *JV*-chatacteristics for Ge-Sb-Te HJs formed on n-type silicon before implantation (▲,△) and subjected to different doses of the Bi implant: $5x10^{14}$ cm^{-2} (□,■), $1x10^{15}$ cm^{-2} (◆,◇), $3x10^{15}$ cm^{-2} (▼,▽). Open symbol and filled symbols correspond to 300K and 77K, respectively.
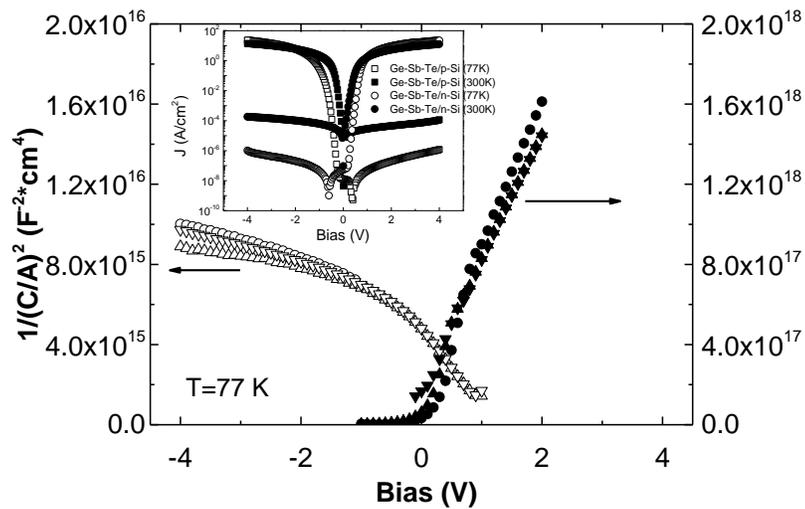

Figure 4. Mott-Schottky plots for unimplanted Ge-Sb-Te formed on n-type (open symbols) and p-type (filled symbols) silicon measured at frequencies of 100 kHz (○,●), 200 kHz (▲,△), 400 kHz (▼,▽), and 1 MHz (◆,◇) at 77K. The inset shows *JV*-curves taken at 300K (filled symbols) and 77K (open symbols).

Bi dose (cm^{-2})	Ge-Sb-Te							
	Net free carrier concentration N (cm^{-3})		V_{fb} (V)		V_c (V)	N_t (cm^{-3})	N_{it} ($10^{12}\cdot$cm^{-2})	ε
	p-Si	n-Si	n-Si HJ	p-Si HJ				
	3.1×10^{15}	1.9×10^{13}	1.2	-0.3	1.27	1.7×10^{16}	0.1	12
5×10^{14}	4.2×10^{15}	3.9×10^{15}	1.0	-1.7	4.5			
1×10^{15}	6.4×10^{15}	1.7×10^{15}	7.0	-3.2	5.7			
3×10^{15}	7.0×10^{15}	7.9×10^{14}	5.3	-3.0	5.9	1.07×10^{18}	2.4	16.5

Table 1. Doping in silicon substrate N, the flat band voltage V_{fb}, the critical voltage V_c, the total interface trap density N_{it}, the trap density N_t, and the relative permittivity for the Ge-Sb-Te and the Ga-La-S films on silicon as influenced by implantation of Bi.

4. CONCLUSIONS

To conclude, ion implantation of bismuth in GeTe and Ge-Sb-Te modifies the electrical properties of the films to very different extent. Along with modification of the chemical composition of a target material, ion-implantation induces defects, which change the conductivity of the films. The weak temperature dependence of the thermopower coefficient in ion-irradiated samples is indicative of the charge-carrier path being via localized states. The variations in conductivity are accompanied by a large increase in the defect density in amorphous chalcogenide films, as inferred from the analysis of the space-charge limited current. Considering relatively low interface trap density, at least in the un-implanted samples, rectification is likely to be controlled by a net negative charge in the chalcogenide films. In respect to passivation, the interfaces trap density in the Ge-Sb-Te/Si HJs before the bismuth implantation is ~10^{11} cm^{-2}eV^{-1}. Implantation of Bi results in the flat-band voltage shift, which is larger for the case of n-type devices. This suggests the increase in the total trap densities in the Ge-Sb-Te/Si interface is partially due to formation of acceptor-like interface states.

5. ACKNOWLEDGEMENTS

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