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First-principles study of sulfur passivation of GaP(001) surface at one-monolayer coverage

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Using first-principles total energy method, we have studied the structural and electronic properties of Ga- and P-terminated GaP(001)(1×2) surfaces adsorbed with one monolayer of sulfur. It was found that the sulfur atoms prefer to occupy bridge sites and the periodicity becomes (1×1) on both Ga- and P-terminated surfaces. The S-Ga bond was confirmed to be stronger than the S-P bond. The electronic analysis showed that the surface state within the energy gap on the Ga-terminated GaP surface was noticeably reduced by the sulfur adsorption, while such reduction does not occur on the P-terminated surface due to the S-P antibonding state. The nearly filled S dangling bonds on the Ga-terminated surface make this surface resistant to contamination.

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1. Introduction

Chalcogenide passivation of III–V compound semiconductor surfaces has received much attention in recent years due to the achieved improvement of chemical and electronic properties of surface. Generally, chemical passivation makes the surface inert against the oxidation in the atmosphere. Electronic passivation, on the other hand, results in substantial decrease in the surface states within the energy gap and leads to a flat band condition at the surface [1]. Furthermore, passivation effect on the semiconductor surfaces leads to decreased Schottky barrier and improved device characteristics.

Experimentally the structures of sulfurized III–V semiconductor surfaces have been studied by low-energy electron diffraction (LEED) [2-4], scanning tunneling microscopy (STM) [5], and reflection high-energy electron diffraction (RHEED) [6,7]. It was found that there exists a transition from (1×2), (1×1) to (2×1) structures, and sulfuration of semiconductors removed the oxide layer from the surface and formed a thin sulfide coating on it. Theoretically, the sulfur adsorption on GaAs (001) and InP(001) surfaces at different coverages have been investigated based on density-functional theory (DFT)[8-14]. These results showed that the most stable structure consists of the cation-terminated surfaces and the sulfur atom is mainly bonded with the cation atoms. Also, the surface states within the energy gap were substantially reduced upon sulfur adsorption.

So far, the passivation effect of sulfur adsorption on the GaP(001) surface has attracted several experimental studies. Fukuda and his co-workers [5,15-19] have studied structural and electronic properties of S-covered GaP(001) surface by means of LEED, STM, Auger electron spectroscopy (AES), inverse and ultraviolet photoemission spectroscopy (IPES and UPS), x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). A (1×1) structure was observed with H_2S treatment at room temperature for the coverage of one monolayer (ML) [6,16,17], and a (1×2) structure appeared with the treatment at 450℃ at half a monolayer [5]. The XPS and STM studies suggested that sulfur atoms only bond to gallium atoms and sit at the bridge sites. The electronic property of the (1×1) structure was investigated by Fukuda et al. employing the IPES technique [16], in which it was indicated that the passivation of GaP(001) with H_2S was effective for strong reduction of the unoccupied surface states in the band gap. On the other hand, Lu *et al.* have studied the passivation effect of the GaP(001) surface with the basic $(NH_4)_2S$ treatment [20]. The crystal structure of S-covered Ga-terminated GaP(001) (1×1) surface was obtained, and the XPS showed that no P-S bonding was detected on passivated surface, similar to the case of H_2S treatment. However, with the neutralized $(NH_4)_2S$ solution treatment, Yuan *et al.* found that the stable P-S bonding was formed on the surface [21], in line with the passivation effect of $(NH_4)_2S_x$ treatment [6]. Therefore, the passivation mechanism on the GaP(001) surface has not been clearly understood yet. Furthermore, no theoretical studies of the

S passivation of GaP(001) surface by first-principles calculations have been reported up to now.

In this work, we presented an *ab initio* investigation of structural and electronic properties of the S adsoption on GaP(001) surface at 1 ML coverage. The Ga- and P-terminated surfaces have been taken into account to elucidate the bonding character. To explain the stability of different surfaces and present the distribution of the surface state density, we analyzed the electronic band structure based on the tight-binding picture. The surface phase diagram at different coverages observed experimentally was confirmed in the present work. We also found that the structures are comparable to those of S-adsorbed InP(001) (1×1) and GaAs(001) (1×1) surfaces.

2. Calculation method

Our calculations were carried out within the DFT framework using VASP code. The electron–ion interaction was described by projector augmented wave method (PAW) [22]. We employed the generalized gradient approximation (GGA) using the exchange-correlation functional according to Perdew and Wang [23,24]. The electronic ground state was calculated with the residuum-minimization techniques. The geometric structure was optimized with the conjugated-gradient technique. The wave functions have been expanded in plane waves with a cutoff energy of 450 eV. Integration over an irreducible Brillouin zone was carried out using the Monkhorst-Pack grid of 6×6×1 for the geometry optimization and 10×10×1 for the electronic-structure calculation at the equilibrium volume. The unit cell consists of five (001) crystal layers of GaP and a vacuum region equivalent to six layers between any two consecutive slabs. The sulfur adatoms were adsorbed on only one surface of the slab. The bottom two layers of the slab were fixed at the ideal positions for simulating a bulk-like termination, while the three topmost layers of the slab and the S adatoms were completely relaxed during geometry optimization. In all the calculations hydrogen atoms with charge of $0.75\left|+e\right|$ and $1.25\ \left|+e\right|$ were used to saturate the phosphorus (gallium) dangling bonds on the surface of the slab without adsorbate. A planar dipole layer in the middle of the vacuum region as introduced by Neugebauer and Scheffler was also considered [25]. The calculated equilibrium lattice constant of 5.50 Å was used throughout the calculations.

3. Results and discussion

3.1. Structural parameters

When a full monolayer of S adatoms were adsorbed on the Ga- and P-terminated GaP(001)(1×2) surfaces, we considered seven possible adsorption sites: namely, $S_{HB}+S_{HH}$, $S_{HB}+S_{T3}$, $S_{HB}+S_{T4}$, $S_{HH}+S_{T3}$, $S_{HH}+S_{T4}$, $S_{T3}+S_{T4}$ and $S_{sub}+S_{sub}$ (see FIG.1). The S_{HB}, S_{HH}, S_{T3}, S_{T4} and S_{sub} denote that the adatoms occupy the bridge, pedestal, valley bridge (on top of a third-layer atom), cave (on top of a fourth-layer atom) sites, and surface substitute site, respectively. The structures of all the possible adsorption systems have been optimized and the adsorption energies have been calculated. The adsorption energy is defined by the formula $E=[E_{S/GaP(001)}-E_{GaP(001)}-NE_S]/N$, where $E_{GaP(001)}$ and $E_{S/GaP(001)}$ are the total energies of a clean GaP(001) surface and the adsorbate system, respectively, N is the number of sulfur atoms, and E_S is the total energy of a spin-polarized free sulfur atom. Our results showed that the $S_{HB}+S_{T4}$ model is preferred for both Ga- and P-terminated GaP surfaces. It is also observed that all Ga (or P) dimers are broken at a full monolayer with the periodicity changing from (1×2) to (1×1), consistent with the experimental observation under vacuum-annealing [6]. Sulfur atoms were found to occupy bridge sites, while Ga and P atoms moved to bulk-like positions. For one S monolayer adsorbed on the Ga-terminated GaP(001) (1×1) surface, the S-Ga bond length is calculated to be 2.33 Å, and the S-Ga vertical distance is 1.28 Å. The Ga-S-Ga bond angle is obtained to be 112.48°. These results are comparable to the S-adsorbed Ga-terminated GaAs(001) (1×1) surface (S-Ga bond length:2.27Å) [26,27] and S-adsorbed In-terminated InP(001) (1×1) surface (S-In vertical distance:1.30 Å , In-S-In bond angle:113.8°)[28]. In case of the P-terminated GaP(001)(1×1) surface covered with 1ML S overlayer, the S-P bond length is calculated to be 2.22 Å, comparing with the S-As bond length of 2.30 Å on the S-covered As-terminated GaAs(001)(1×1) surface[26,27]. The P-S-P bond angle is obtained to 121.93° and the interplanar distance between the S and P atomic layer is 1.08 Å. In addition, for the $S_{HB}+S_{T4}$ model, the adsorption energy of the Ga-terminated surface is 0.99 eV lower than that of the P-terminated surface, indicating that the S-Ga bond is more stable than the S-P bond. This may be attributed to the fact that the S-P bond contains 2.25 electrons and the S-Ga bond has 2.0 electrons [27]. The excess electrons weaken the S-P bond by occupying an antibonding state. Our finding agrees well with the experimental observation that the number of S-P bonds are decreased and S-Ga bonds are dominated with the increasing annealing temperature [6].

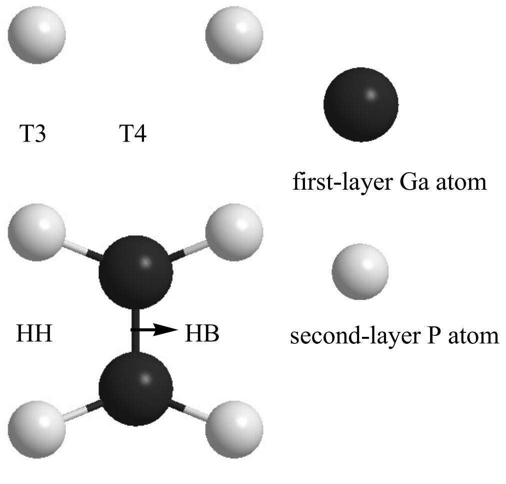
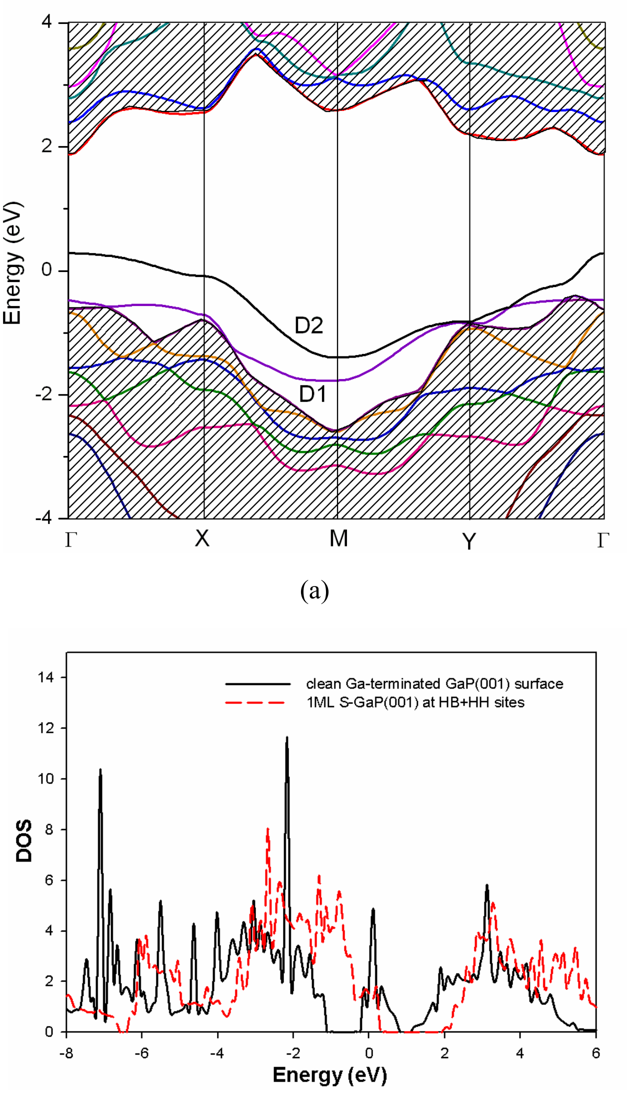


Fig. 1. Schematic plane view of the different adsorption sites for sulfur adsorption on the Ga-terminated GaP(001)(1×2) surface. HH, T3, HB, T4 sites are indicated.



(a)

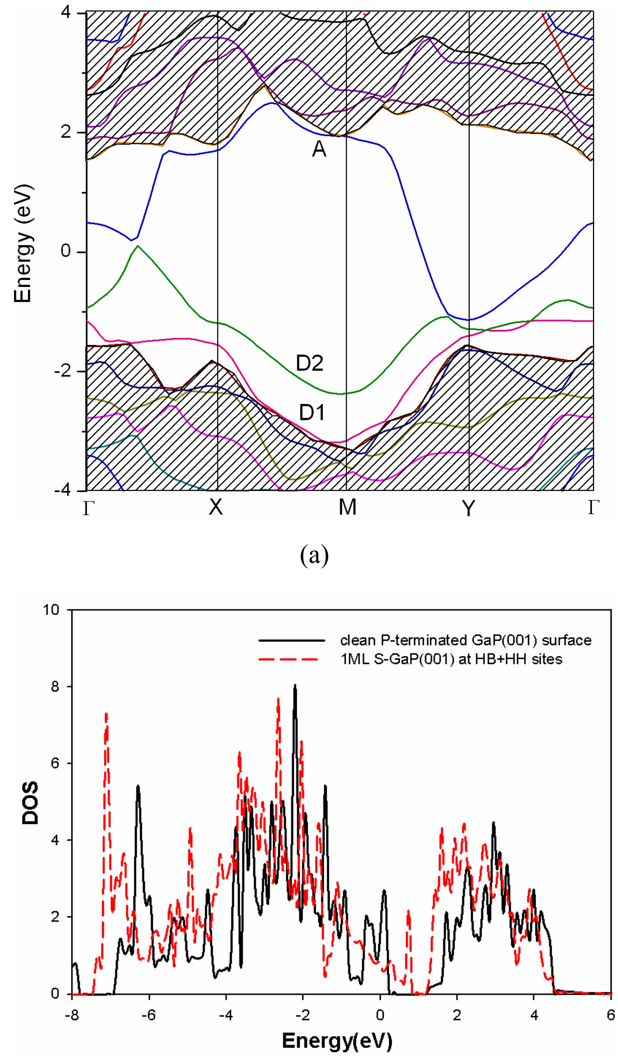
(b)

Fig. 2. Electronic structure of the Ga-terminated GaP(001) (1×1) surface with 1ML S adsorbed on the optimized bridge site. (a) electronic band structure (b) the total density of states.

In the case of S_{sub}+S_{sub} model, S-S dimer is formed. For the S-S dimer on the P-terminated GaP(001)(1×2) surface, the optimized geometry showed that the dimer was broken and the periodicity changed to (1×1), consistent with sulfur adsorption at the S_{HB}+S_{T4} sites. It can be explained by the fact that, as mentioned below, the S dangling bond is completely filled at the S-adsorbed P-terminated surface. For the S adsorption on the Ga-terminated surface, the S dangling bond is partially occupied and the driving force of the dimerization exists. Thus, the surface S atoms can be dimerized, which was also suggested in the case of 1ML S adsorption on Ga-terminated GaAs(001) [27] and In-terminated InP(001) surfaces [28,29]. The S-S dimer bond length is determined to be 3.44 Å and the Ga-S bond length is 2.33 Å. These values are smaller than the corresponding values of S-S dimer on the In-terminated InP(001)(1×2) surface due to the larger radius of In atoms.(S-S:3.80 Å, S-In:2.38 Å) [28]. The calculated adsorption energies showed that there is no energy gain upon dimerizaton of S adatoms, similar to the case of S adsorption on InP(001) surface. However, in the case of In-terminated InP(001)(2×2) surface, the model of two S-S dimer with different bond lengths was found to be the most stable [29,30]. For comparison we also investigated the Ga-terminated GaP(001)(2×2) surface absorbed with two S-S dimer . The results showed that the adsorption energy per S adatoms is larger by 0.70eV than that of the Ga-terminated GaP(001)(1×1) surface adsorbed with 1ML sulfur.

3.2. Electronic properties

Based on the optimized structures, we also investigated the electronic properties of the most stable configurations of sulfur adsorption on the Ga- and P-terminated surfaces. Fig.2 (a) shows the electronic band structure of the Ga-terminated GaP(001)(1×1) surface with 1ML S adsorbed at bridge site. The electronic structure is found to be similar to that of the S-adsorbed In-terminated InP(001)(1×1)[28] and Ga-terminated GaAs(001)(1×1) surfaces [27]. The tight-binding picture suggested that the interaction between the Ga dangling bond with 0.75 electrons and the S sp^3 orbitals leads to the formation of a bonding and an antibonding state [27]. The bonding state, which is contributed by the S-Ga covalent bond, is completely filled and located within the GaP valence bands. On the other hand, the antibonding state is empty and lies within the conduction bands. This makes each surface S atom leave two dangling bonds with 1.75 electrons. The D1 and D2 bands, as shown in Fig.2 (a), are both resulted from the S dangling bonds. The lower D1 band is fully filled and the upper D2 band is partially occupied with 1.5 electrons. The partially filled D2 band shows the possibility of the formation of S-S dimer and reconstruction of (2×1) surface, which confirmed the experiments [6]. The energy gap at Γ is obtained to be 1.61 eV. In Fig.2 (b), we present the total density of states (DOS) of the S-adsorbed Ga-terminated GaP(001) (1×1) surface. The Fermi level of the considered system was set to 0 eV. It is found that the energy gap of the S-adsorbed surface is larger than that of the clean surface. Such finding is reasonable since the S potential is much deeper than the Ga potential [27]. Around the Fermi level, the intensity of the peak is remarkably lowered compared to that of the clean surface. The unoccupied surface states of the clean surface ranged from 1.18 to 1.99 eV are removed upon sulfur adsorption, agreeing well with the experimental results that the surface state at about 1.5 eV is tremendously reduced by sulfur adsorption [16]. The decrease of surface state density, indicative of the improvement of the surface electronic properties, may be ascribed to the S-Ga bond on the passivated surface. For the energy range between 3.26 and 6 eV within the unoccupied states, the intensity of DOS is increased due to the strong s-p hybridization. This is consistent with the IPES spectra observation of the increase in intensity at about 3 eV above the Fermi level upon sulfur adsorption [16]. In the case of S-covered Ga-terminated GaP(001)(1×1) surface, the surface states around the Fermi level are mainly contributed by the S-p states, corresponding to the D2 bands, while the surface states around the Fermi level of the clean surfaces are mainly stemmed from Ga-s and Ga-p states. It is indicated that the S-p, Ga-s and Ga-p states are all involved in the charge redistribution.



(a)

(b)

Fig. 3. Electronic structure of the P-terminated GaP(001) (1×1) surface with a S monolayer adsorbed on the optimized bridge site. (a) electronic band structure (b) the total density of states.

The electronic band structure of the P-terminated GaP(001)(1×1) surface with 1ML S adsorbed at bridge sites is presented in Fig.3(a). Similar to the Ga-terminated surface, the interaction of the P dangling bonds with 1.25 electrons and the S sp^3 orbitals results in the formation of a bonding and an antibonding state, and the S dangling bonds contribute to the D1 and D2 bands. But the S dangling bond is completely filled and the P-S antibonding state is not empty but partially filled with 0.25 electrons. In addition, the P-S antibonding state, which is indicated by the A band in Fig.3(a), is located within the energy gap. It has a large dispersion nearly crossing the GaP energy gap, indicating that the surface state density of the S-adsorbed P-terminated GaP(001)(1×1) surface is almost not reduced in the mid-gap region. This can be confirmed by the DOS distribution in Fig.3(b). The DOS curve shows that one peak around 0.74 eV, corresponding to the antibonding band A and composed of S-p, P-s, P-p orbitals, exists in the energy gap of the clean surface, although the peak strength at the Fermi level is decreased.

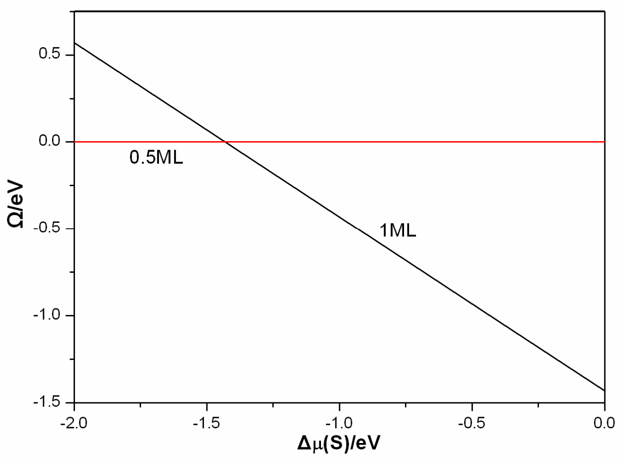


Fig. 4. Chemical potential dependent surface formation energies for the (1×2) and (1×1) reconstructions that S forms on the Ga-terminated GaP(001) at half- and one-monolayer coverage, respectively.

Also, we have estimated the S-induced work-function change, ΔΦ, of the GaP(001) (1×1) phase, which is defined as $\Delta\Phi = \Phi_{\text{S-substrate}} - \Phi_{\text{substrate}}$, where $\Phi_{\text{S-substrate}}$ and $\Phi_{\text{substrate}}$ are the work function of the system with and without S adsorbate, respectively. The changes of work-function due to S adsorption are found to be 1.9 and 0.38 eV for the Ga-terminated and P-terminated surfaces, respectively, suggesting that some charge is transferred from the substrate to the S adsorbate. Such phenomenon may be caused by the fact that the electronegativity of S is higher than that of Ga and P, which leads to a negative dipole (pointing inward) and increased work function [31].

3.3. Surface phase diagram

As mentioned above, the Ga-terminated GaP(001)(1×1) surface absorbed with one monolayer of sulfur is the most stable structure, and its surface states within the energy gap are markedly reduced by the S adsorption. Structural analysis suggested that the (1×1) pattern can be transformed from (1×2) pattern as the coverage increases from 0.5 to 1 ML, consistent with the experiments [6]. In this work, we also modeled this transition.

The experimental results showed that the most stable structure of the GaP(001)(1×2) surface adsorbed with 0.5 ML S is the sulfur atoms bonding to gallium atoms at the bridge sites between the gallium dimmer [6]. To compare the stability of the (1×2) and (1×1) structures, we calculated the surface formation energy, which is dependent on chemical potential and is defined as follows:

$$\Omega = E_{tot} - \sum_i \mu_i N_i ,$$

where E_{tot} denotes the total energy of a given slab configuration, μ_i and N_i are the chemical potential and number of atoms of constituent i, respectively. The surface formation energy of (1×2) structure was set to be zero, and then Ω of (1×1) structure can be expressed as

$$\Omega = E_{1ML} - E_{0.5ML} - \Delta\mu(S) - \mu_{Sbulk} ,$$

where E_{1ML} and $E_{0.5ML}$ are the total energy of the (1×1) and (1×2) structures, respectively. $\Delta\mu$(S) is defined as the difference between the sulfur chemical potential (μ_S) and the energy per bulk sulfur atom(μ_{Sbulk}). Our results are summarized in the Fig.4. It is clearly shown that the (1×1) structure is more stable when $-1.34\text{eV} < \Delta\mu(S) < 0$, and the (1×2) phase is changed to the (1×1) phase at the $\Delta\mu$(S) of -1.34eV. These results agree well with the experimental findings [6].

4. Summary

In conclusion, the structural and electronic properties of 1ML S adsorption on the Ga- and P- terminated GaP(001)(1×2) surfaces were investigated by DFT–GGA method. Our calculations showed that sulfur atoms prefer to adsorb at the bridge sites and the periodicity becomes (1×1) on both the Ga- and P-terminated surfaces. The S-Ga bond is stronger than the S-P bond. The calculated structural properties are found to agree well with available experiments and are comparable to S-adsorbed InP(001)(1×2) and GaAs(001)(1×2) surfaces. Our analysis of electronic properties showed that the surface state density in the mid-gap region of the Ga-terminated GaP(001) surface was noticeably reduced by the sulfur adsorption, while such reduction did not occur on the P-terminated surface due to the S-P antibonding state within the energy gap. We suggest that the S-Ga bonds are dominantly formed at the S-covered GaP(001) surface. The work-function changes due to S adsorption were predicted to be 1.9 and 0.38 eV for the Ga- and P-terminated GaP surfaces, respectively. Also, the phase transition from (1×2) to (1×1) pattern was modeled in this work. It turns out that the (1×1) structure is more stable than (1×2) phase when $-1.34\text{eV} < \Delta\mu(S) < 0$, and the (1×2) phase is transformed into the (1×1) phase at the $\Delta\mu$(S) of -1.34eV. These results agree well with the experimental findings. We hope this work can provide a better understanding of the nature of chemical bonding between S and substrates and the electronic properties of the S-adsorbed GaP(001)(1×1) surface, which is of great benefit to producing good quality GaP(001) surface for electronic applications.

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