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N_2 plasma interaction with molybdenum disulfide monolayers

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Based on ab initio DFT simulation results, the main processes of the interaction of thermal N atoms with MoS_2 monolayers are revealed, potential mechanisms of defect formation by low-energy ions N_2^+ are described, and the ion threshold energy required to sulfur removal is estimated.

Keywords: molybdenum disulfide, monolayer, plasma, radicals, ions, simulation.

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Owing to a unique combination of electronic, optical, mechanical, and thermal properties, 2D materials are regarded as the most promising candidates for nanoelectronics applications. Quasi-two-dimensional molybdenum disulfide (MoS_2), which has a bandgap dependent on the number of layers, the applied mechanical stress, and the acting electric field [1–3], is one material of this kind that attracts considerable attention. Although low-temperature plasma is used often in the production of electronic components, plasma particles (ions and radicals) may cause considerable damage to ultrathin materials of this type, inducing unwanted changes in their properties (in particular, via surface functionalization) [1,4–7]. Data collected in experiments on irradiation of ultrathin MoS_2 films with N_2 plasma [8] demonstrated that N_2^+ ions of even a fairly low (20–25 eV) energy induce noticeable damage to MoS_2 films, causing partial destruction of several upper MoS_2 layers (although the indicated ion energy appears to be insufficient for physical sputtering of this material). Thermal N atoms (remote N_2 plasma) modify only the upper layer of films by removing a fraction of sulfur and substituting it with nitrogen [5,8]. X-ray photoelectron spectra of irradiated samples revealed that the peaks of molybdenum Mo3d and Mo3p were altered considerably in the course of irradiation, but the primary S2p sulfur peak remained unchanged. This is indicative of the formation of Mo−N bonds on the surface and of a low probability of S−N bond formation. It should be noted that the damage of samples processed with thermal O atoms (remote O_2 plasma) in similar conditions was more significant: all the mentioned peaks were altered (i.e., both Mo−O and S−O bonds formed) [6–8].

In the present study, the interaction of thermal N atoms and low-energy N_2^+ ions with a MoS_2 monolayer is simulated using the quantum-mechanical density functional theory (DFT) method in order to identify the key mechanisms of elementary physicochemical processes that accompany this interaction. Static and dynamic DFT calculations were performed within the generalized gradient approximation (GGA) with the PBE exchange-correlation functional in the plane wave basis with PAW pseudopotentials in VASP [9]. Computational resources of the supercomputer complex at the Moscow State University [10] were used.

It has been demonstrated in earlier DFT simulations [11] that a nitrogen atom may be adsorbed in the „top" position above a sulfur atom on the surface of a defect-free MoS_2 monolayer. A Mo_3−SN surface group with a weak S−N bond $d = 1.54$ Å in length forms as a result (Fig. 1, a), and a certain redistribution of the electron density is observed. This is reflected in the values of partial charges Q, but induces almost no structural changes in the monolayer (see the table). However, the results of static DFT calculations performed for a given magnetic moment of the system revealed that chemisorption is possible for excited states of atoms N^* (metastable $N(^2D)$, $N(^2P)$), while physical sorption at a distance of ~ 3 Å from the top of the monolayer is prevalent for N atoms in the ground $N(^4S)$ state. Therefore, just as in other interactions with various molecules and surfaces (see, e.g., [12,13]), scattering is the most likely mechanism of interaction of thermal ($E_0 \approx 0.03$ eV) $N(^4S)$ atoms in real-world conditions. This assumption was verified in dynamic DFT simulations: following calculated trajectories, $N(^4S)$ atoms with a low (0.03–0.3 eV) initial energy underwent scattering off a defect-free MoS_2 surface,

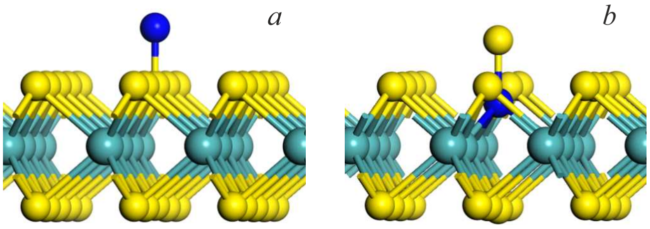

Figure 1. Surface groups Mo_3−SN (a) and Mo_3−NS (b) that may form on the surface of a MoS_2 monolayer as a result of chemisorption of a nitrogen atom. Mo, S, and N atoms are colored cyan, yellow, and blue, respectively. A color version of the figure is provided in the online version of the paper.

Parameters of adsorption of a nitrogen atom on a MoS_2 monolayer without defects and with an S vacancy

Adsorption result	Binding energy E_{bind}, eV	Interatomic distance d, Å		Partial charge Q, e		
		Mo–S	S–N	Mo	S	N
			Monolayer without defects			
–	–	2.425	–	+0.22	−0.11	–
Mo_3–SN group	−1.6	2.451	1.539	+0.22	+0.03	−0.24
Physical sorption	−0.05	2.425	~ 3.0 (above the surface)	+0.22	−0.11	−0.03
Mo_3–NS group	−2.9	2.430	1.682	+0.26	−0.01	−0.25
			Monolayer with an S vacancy			
S vacancy	–	2.396	–	+0.21	–	–
Mo_3–N group	−5.8	2.446	2.025, 2.023	+0.28	–	−0.32

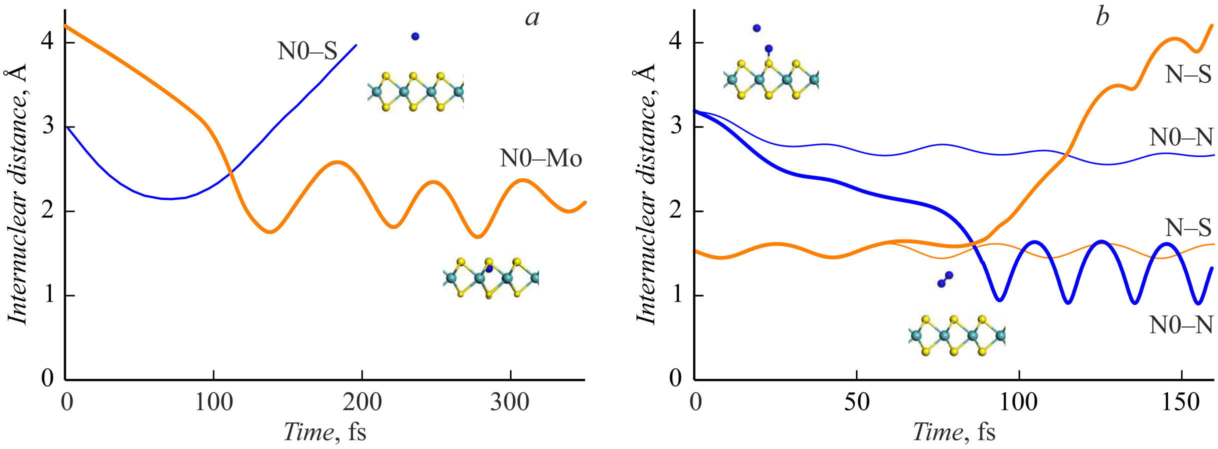

Figure 2. Temporal dependences of distances between N, S, and Mo atoms for different processes of interaction between an incident N atom (denoted as N0) with energy E_0 and the surface of a MoS_2 monolayer. *a* — Scattering off a defect-free monolayer at $E_0 = 0.3$ eV (curve corresponding to distance N0–S) and adsorption into S vacancies at $E_0 = 0.1$ eV (curve corresponding to distance N0–Mo); *b* — scattering off a surface group at $E_0 = 0.05$ eV (thin curves for N0–N and N–S) and recombination of incident and adsorbed atoms at $E_0 = 0.3$ eV (thick curves for N0–N and N–S).

transferring 20–40% of their initial energy to it. The temporal dependence of the distance between incident atom N0 and the surface S atom closest to it (curve N0–S in Fig. 2, *a*) illustrates the scattering process.

Of special note are the following two major findings made in simulations of the impact of individual N atoms. The first one concerns the formation of a Mo_3–NS surface group with a nitrogen atom displacing a sulfur atom and positioning itself at a lattice site (Fig. 1, *b*). This configuration emerged at an initial energy of ~ 10 eV of an incident N atom in dynamic calculations and when a nitrogen atom was positioned in the immediate vicinity of the surface (which is possible if an atom has a sufficient additional energy) in static calculations. The second finding is that the emergence of defects on the surface of a monolayer leads to a considerable enhancement of the chemisorption probability: specifically, an incident N atom in both ground and excited states is adsorbed easily into a vacancy (formed as a result of removal of a sulfur atom) with the formation of significantly stronger Mo–N bonds (Fig. 2, *a*).

The results of DFT calculations also revealed that adsorbed N atoms on the surface do not raise the probability of further adsorption of atoms. A thermal N atom is attracted strongly to a Mo_3–SN surface group, and a N_2 molecule may form as a result. The number of adsorbed N atoms did not exceed 2 in static calculations for a model of 4×4 lattice cells (with 16 S atoms acting as possible adsorption centers). The corresponding maximum degree of nitrogen coverage of a defect-free monolayer is $\sim 10\%$. In dynamic calculations, recombination of incident and adsorbed N atoms with the formation of N_2 molecules was observed when the initial kinetic energy of the incident atom exceeded ~ 0.2 eV (Fig. 2, *b*). Notably, the recombination probability increased with increasing incidence angle (specifically, recombination occurred at 0.1 eV when the angle was 60°). Intriguingly, almost the entire energy released as a result of recombination was

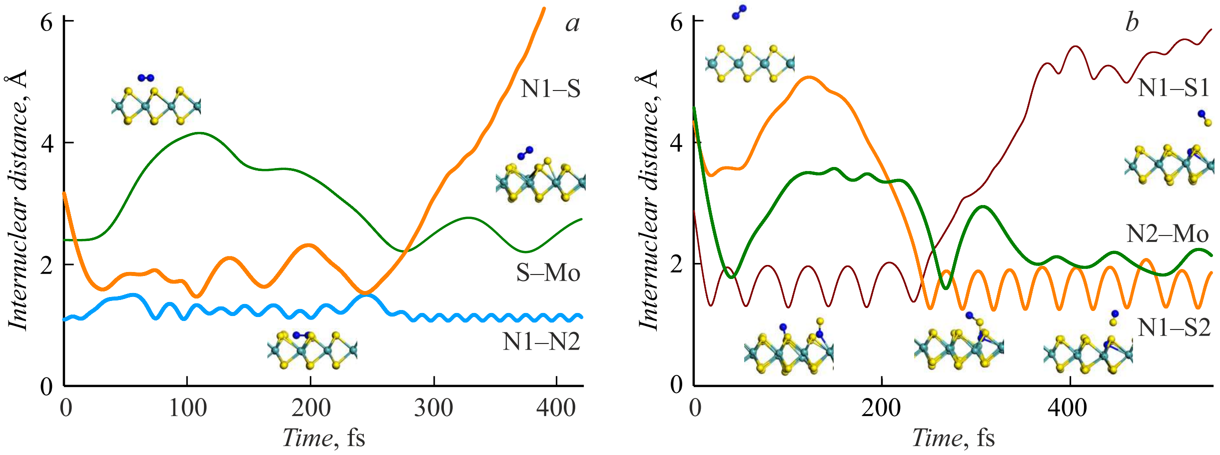

Figure 3. Temporal dependences of distances between N, S, and Mo atoms in the interaction of an incident N_2^+ ion (its atoms are denoted as N1 and N2) with the surface of a MoS_2 monolayer. *a* — Scattering off a defect-free monolayer at $E_0 = 15\,eV$; *b* — formation of a Mo_3-N surface group and a volatile SN radical at $E_0 = 20\,eV$.

transferred to forming N_2 molecules that left the surface in a highly excited rotational–vibrational state. Chemisorption on the surface of a monolayer is possible for thermal excited N^* atoms. Their flux in experimental conditions [8] is considerably (by an order of magnitude or more) lower than the flux of $N(^4S)$ atoms. In addition, chemisorbed atoms (both on a defect-free surface and in *S* vacancies) recombine fairly easily with incident atoms, thus reducing the density of $S-N$ bonds on the MoS_2 surface. This agrees well with the results of analysis of X-ray photoelectron spectra [8].

Similar calculations were performed for N_2^+ ions with an energy of $5-25\,eV$ in order to study the mechanisms of monolayer destruction under irradiation with N_2 plasma. Dynamic DFT simulations revealed that energy $E_0 = 5 - 10\,eV$ of incident N_2^+ ions was not sufficient to produce stable defects on the MoS_2 surface; notably, the ion–surface interaction was very fast with a characteristic time scale of $\sim 50 - 100\,fs$. At initial energy $E_0 = 15\,eV$, the interaction pattern changed (see Fig. 3, *a*): the impact of an ion induced a significant extension of an $N-N$ bond (curve $N1-N2$) and displaced S atoms from equilibrium positions (curve $S-Mo$), but displaced atoms returned within $150-200\,fs$ in the majority of calculated trajectories, and an N_2 molecule was restored. It is notable that the average fraction of energy transferred to a monolayer was $\sim 60 - 70\%$ in the examined cases and an N_2 molecule was in a highly excited rotational state after the impact. A further increase in the energy of an incident N_2^+ ion (to $20-35\,eV$) induced dissociation of the incident particle upon impact and noticeable structural changes in a monolayer: surface groups Mo_3-NS or Mo_3-N emerged on the surface, which was accompanied in certain cases by detachment of an SN radical (Fig. 3, *b* illustrates the latter process). Therefore, the process of defect formation and substitution of sulfur with nitrogen is accelerated greatly under the influence of ions. Besides, it was demonstrated experimentally [5] that additional mechanical stresses, which may induce cracking and cause further damage to material layers, are produced in samples with a high concentration of interstitial nitrogen.

Thus, the obtained simulated data suggest that scattering and physical sorption at a sufficient distance (~ 3Å) from the surface are the primary processes occurring in interaction between thermal N atoms in the $N(^4S)$ ground state and the surface of a defect-free MoS_2 monolayer, while N^* atoms in the $N(^2D,^2P)$ excited state may undergo chemisorption above S atoms, forming Mo_3-SN surface groups with weak $S-N$ bonds. The incidence of additional N atoms in both ground and excited states onto a monolayer near Mo_3-SN surface groups may result in the formation of N_2 molecules and reduce the surface concentration of nitrogen. Thermal N atoms are incorporated easily into vacancies forming after the removal of sulfur, but may also recombine with subsequent incident atoms. Incident N_2^+ ions with an energy of $20-35\,eV$ induce an intense process of defect formation on the monolayer surface and substitution of sulfur with nitrogen.

In practical terms, this simulation demonstrated the difficulty of achieving a high degree of MoS_2 doping with nitrogen (up to a complete substitution of the upper sulfur layer with nitrogen) through remote N_2 plasma surface treatment. When a flux of thermal N atoms is used for irradiation, additional initiation of the removal of S atoms by electron-excited (N^*) and/or impurity particles (e.g., O atoms that may enter a reactor due to inleakage of air and dissociation of O_2 molecules; both nitrogen and oxygen components will be present in the upper layer of samples in this case) and sample heating is needed. Precision control of the ion energy is crucial in plasma processing of ultrathin MoS_2 films, since ions may induce the formation of vacancies and other defects that exert a considerable influence both on the properties of films themselves and on the processes of their interaction with radicals.

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Conflict of interest

The authors declare that they have no conflict of interest.

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