

A Case Report: Dissipation of The Excess Energy of the Adsorbate-Thermalization *via* Electron Transfer

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Abstract

In the following article, the author has theoretically proved that energy dissipation during surface reaction is an important part of the studies of surface reaction and catalysis. The magnitude of the problem is staggering as the energetic effect of adsorption at surfaces frequently reaches several electronvolts. The two basic scenarios were identified: dissociative adsorption in which the products are attached at the surface sites or the abstractive process in which only one atom is attached at the surface whereas the second is ejected in the vacuum carrying out the energy excess.

Keywords: *Electrons; Adsorption; Kinetic energy*

Introduction

Energy dissipation during surface reaction is an important part of the studies of surface reaction and catalysis [1]. The magnitude of the problem is staggering as the energetic effect of adsorption at surfaces frequently reaches several electronvolts [2,3]. The two basic scenarios were identified: dissociative adsorption in which the products are attached at the surface sites, or the abstractive process in which only one atom is attached at the surface whereas the second is ejected in the vacuum carrying out the energy excess. The dissociative process channels includes kinetic energy dissipation by creation of electron-hole pairs [4], excitation of phonon bunches, or persistence of “hot” adatoms, i.e. high energy atomic products at the surface [5]. The abstractive process is observed during adsorption of F₂, Cl₂ and Br₂ at silicon surfaces [6]. Unfortunately, the experimental evidence does not confirm any of these hypotheses, giving mixed responses, depending on the adsorbate and the surface.

Case Report

A new scenario of the thermalization process of the adsorbates at solid surfaces was devised and described [7]. A crucial component of the scheme is the surface electric dipole layer in which the electron wavefunctions extend over the positive ions thus creating strong local electric field which accelerates the electrons into the solid interior and the positively charged atoms/molecules in the opposite direction. The case study of the polar aluminum nitride surfaces, both AlN (0001) and AlN (000 $\bar{1}$) by *ab initio* calculations shows that such field may induce potential difference of about 10 V over the distance of 2 nm. It is therefore proposed that approximating species, atoms and molecules alike, lose their electrons in such strong electric field which tunnel into the solid interior, acquiring the excess kinetic energy in the above mentioned electric field. The electron escape into the solid interior charges the approaching atom/molecule positively so it is retarded by the local electric field, reducing its kinetic energy. Finally the atoms/molecules are located smoothly into the adsorption sites.

Discussion

According to the proposed scenario, the excess energy of the electron is not dissipated locally, avoiding melting or creation of defects as the adsorption experiments show. The tunneling electrons penetrate deep into the solid interior losing its kinetic energy by emission of phonons during travelling in the lattice of bulk crystal. The critical for the effective dissipation of the excess energy of the adsorbate is the time needed for tunneling of the electron into crystal interior. The scenario is supported by the *ab initio* calculation results including density function theory of the slabs representing AlN surface and the Schrodinger equation for time evolution of hydrogen-like atom at the solid surface. The case study of hydrogen atom approaching AlN (0001) surface was used for solution of time dependent Schrodinger to find the probability of tunneling of electron. The atom was positioned at the distance of 1.5 nm from the surface. It was shown that considerable transition probability is attained after $\tau_{jump} \approx 2 \cdot 10^{-15} s$. After slightly longer time of order of $\tau_{jump} \approx 10^{-14} s$, the transition probability attained 0.3 at level it was saturated. The thermal velocity normal component may be obtained from equipartition principle may be obtained from equipartition principle. For physical vapor transport (PVT) growth of AlN at 2500 K the perpendicular component of the average velocity is $v = \sqrt{\frac{k_B T}{2M_N}} \approx 830 m/s$. Assuming the collision process interaction range $d=5\text{\AA}$, the collision time

estimate is: $\tau_{coll} \approx 7 \cdot 10^{-13} s$. The tunneling time is about two orders of magnitude shorter than duration of the typical atom-surface collision process and could be treated as instantaneous. The estimate confirms the possible role of electron transfer and the retardation of the positively charged adatom/admolecule at the final stage of the collision process. It is proposed that the electron transfer is the most likely channel of the excess kinetic energy dissipation during collisions and adsorption at solid surfaces. In the result the positively charged atoms/molecules are slowed down so they could be attached smoothly at the surface of the solid avoiding effects related to large excess kinetic energy. The proposed thermalization process is effective, not leading to creation of defects or melting. These conclusions are consistent with the existing experimental data.

Conclusion

The proposed scenario opens novel possibilities of investigation of the processes that are kinetically controlled and in which the electron transfer plays decisive role. Among them adsorption and catalysis are the most eminent, influencing processes important for many branches of modern technology, affecting manufacturing of large number of products. Application of the presented results may provide deeper understanding of these processes leading to fast progress in many important technologies.

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