Polar AlN surface under nitrification determined by density functional theory

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Principal physical properties and kinetic processes for nitrogen-covered AlN polar Al-terminated AlN(0001) surfaces were determined using density functional theory (DFT) calculations. It was found that both aluminum and nitrogen adatoms induce states in the bandgap. In addition, Al dangling bonds (DB) states are present in the bandgap. The Al-Al bonds related to Al(T4) adatoms are located in the lower part of the bandgap and are completely filled. The upper states are a mixture of Al (DB) states both from Al surface atoms and Al adatoms and are partially empty. In the case of an N adatom, four states emerge in the bandgap, two of which are Al-N bonding states. The other two are Al (DB) states located high in the bandgap. The energy of Al broken bond-related band extends for about 2 eV so that a single energy of the state cannot be defined. The energy which is of interest is the one corresponding to an electric neutrality of the surface and is located about 0.4 eV below the CB. As it was shown, both p- and n-type could be simulated, which is of importance for determination of the adsorption energy . It should be added that a quantum overlap repulsion between the CB states and aluminum DB states increases the energies of the band states at the surface. This additional quantum effect is superimposed at a long-distance variation of the band energy. The latter indicates on an acceptor behavior for p-type and semi-insulating bulk and donor behavior for p-type of the Al broken bond state. The H3 site has the lowest energy, about 2.2 eV lower than the T4 site, which is still energetically more stable than the "on-top" position. The lowest energy quantum states of N adatoms are s states degenerated with the VB, and consecutively two N_{p_x}, N_{p_y} states located in the bandgap. The highest energy p_z state is also located in the bandgap, below an Al broken bond state. The charge during the adsorption of N adatoms transfers electrons from the Al broken bond state to the topmost N adatom states. Molecular nitrogen is adsorbed in a skewed on-top position above the Al surface atom. The electronic states of the admolecule are occupied like in the molecule. It was shown that for a low nitrogen coverage, the Fermi level is pinned by Al broken bond states located below the CBM. Adsorption of atomic nitrogen depends on the Fermi level due to the involved charge transfer. For a low N coverage the adsorption energy is very high, about 7.2 eV/atom. For this coverage the molecular nitrogen adsorption is dissociative with the energy gain of 6.05 eV/molecule. Above 0.25 Ml coverage the atomic nitrogen adsorption energy gain is reduced below 4 eV as the Al broken bond is empty and energy gain from electron transfer is not possible. For such a coverage the adsorption of N_2 is molecular and leads to an energy gain of about 1.5 eV, which is energetically preferred as dissociative process leads to an energy loss. Therefore, the molecular process dominates for a higher nitrogen coverage. An equilibrium pressure of molecular nitrogen above an AlN(0001) surface was also determined. It was shown that the pressure depends critically on the Fermi level position, thus on the nitrogen coverage. For a low nitrogen coverage, the equilibrium pressure is very low, a few orders of magnitude below a typical growth pressure, while for a high coverage the equilibrium pressure is high.