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**Opracowanie nowego modelu strukturalnego ultracienkiej
warstwy azotku żelaza na Cu(001) z wykorzystaniem
lokalnych pomiarów pracy wyjścia, analizy wzorów
dyfrakcyjnych i oddziaływań z tlenem molekularnym**

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Abstract

Iron nitrides constitute the group of artificially-synthesized materials with unique physicochemical properties. First studies on the interaction of ammonia with iron were conducted in the 19th century, and at the beginning of the 18th century the very first patents on steel nitridation – hardening method based on the formation of a thin layer of iron nitrides – were granted. Decades of structural research on various iron nitride phases allowed constructing their phase diagram that includes multiple phases with different nitrogen content. In 1991, the studies of Yutaka Sugita from Hitachi laboratories revealed exceptionally high magnetic saturation of the α'' -Fe₁₆N₂ phase, that exceed the theoretically predicted maximum value (the so-called Slater-Pauling limit). Unfortunately, up to the present day, there is no success in commercial application of this material, mainly due to its difficult synthesis and susceptibility for decomposition into α -Fe₈N and γ' -Fe₄N phases. However, discovery of Sugita initiated the studies on other iron nitride phases. Much attention was paid to the γ' -Fe₄N phase, which is characterized by ferromagnetic ordering, high magnetic saturation per atom and very good electrical conductivity. Due to potential applications in spintronics, thin epitaxial γ' -Fe₄N films grown on single-crystal supports are particularly interesting.

The aim of this dissertation was to grow ultrathin iron nitride islands and films on Cu(001) single-crystal substrate and determine their physicochemical properties. Ultrathin films are the films with a thickness below 1 nm. The selected substrate, thanks to the crystal lattice parameters, is widely used for the epitaxial growth of thin γ' -Fe₄N films. Articles on ultrathin films published so far mostly focus on the structure of iron nitride, with less attention paid to their properties. Of particular interest was the iron nitride monolayer, which – according to the generally accepted structural model – represents the middle atomic plane of the γ' -Fe₄N unit cell, leading to the „Fe₂N” notation.

During the first stage of the studies, the structural model of monolayer iron nitride on Cu(001) was verified. Islands and films of iron nitride were grown using the procedure developed by the research group of Fumio Komori from the University in Tokyo, which includes bombardment of the copper substrate with nitrogen ions, deposition of metallic iron and post-annealing in ultra-high vacuum (UHV). The experiments performed using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) revealed that the obtained islands and films are structurally virtually-identical to the ones reported by the Japanese group. Additionally, the spectrum resembling the electronic density of states close to the Fermi level, recorded using scanning tunneling spectroscopy (STS), was similar to that published in the literature. Notably, STM additionally revealed a small corrugation within the iron nitride atomic structure, which was not observed so far. The chemical composition analysis, performed using X-ray photoelectron spectroscopy (XPS), revealed that the layer contains more nitrogen than expected for the Fe₂N phase, with stoichiometry matching the Fe_{1.3}N composition. Using STS, the work function of iron nitride islands was determined and found to be considerably different from the one calculated theoretically for the Fe₂N. Based on these findings, a new structural model of monolayer Fe_{1.33}N iron nitride on Cu(001) was developed, that includes the presence of an additional nitrogen atom within each Fe₂N unit cell.

Importantly, the work function calculated for such a system agrees well with the experimentally determined value. The model was further verified with LEED-IV measurements and simulations.

The second stage of the studies was devoted to the interaction of $\text{Fe}_{1.33}\text{N}$ islands on Cu(001) with molecular oxygen. The studies were motivated by the unique catalytic properties of iron and its compounds (e.g. oxides). Different stages of the interaction were monitored, from oxygen adsorption at room temperature to oxidation at elevated temperatures that led to the formation of iron oxides at the expense of iron nitride. Even though there are numerous works on the structure and properties of iron nitrides, as well as countless similar publications on iron oxides, reports describing the transformations between these compounds are still lacking. In order to properly interpret the results, reference studies focused on the oxidation of metallic iron on Cu(001) were conducted, using identical conditions as in the case of iron nitride. Structural STM, LEED and XPS investigations revealed different scheme for iron oxides formation in both examined cases. At low oxygen pressures, iron nitride exhibited partial resistance to oxidation, while under elevated pressures the reaction was found to undergo more rapidly for iron nitride, as compared to metallic iron. An additional experiment carried out with the use of quadrupole mass spectrometry (QMS) allowed determining the reactions taking place at the surface of iron nitride during oxidation. The synthesis of two nitrogen oxides was observed: nitrogen (II) oxide (at elevated substrate temperatures) and nitrogen (IV) oxide (at elevated oxygen pressures). The observations allowed suggesting the possible reaction pathways. Moreover, the studies revealed that iron nitride may be oxidizing not only with molecular oxygen, but also water vapor.

Within the performed studies, also the growth of iron oxides on Cu(410) was investigated. The substrate features four-atom-wide terraces of Cu(001) divided by two-atom Cu(110) walls, which favours directional growth of iron oxide islands and influences their shape. The performed experiments constituted preliminary studies to the growth and characterization of iron nitrides on the same support.

The conducted studies allowed verifying and establishing the existing knowledge on ultrathin iron nitride islands and films on Cu(001), and broadening it with new aspects. In particular, a new structural model of monolayer iron nitride was developed and information on the interaction of the compound with molecular oxygen and water vapor was obtained. The results constitute the basis for future applied research focused, for instance, on the development of heterostructures of iron nitrides with different materials for applications in spintronics and catalysis.