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On the cleaning of monocrystalline metallic samples from impurities

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Abstract

The problem of sample cleaning is essential for all the scientists using ultra-high vacuum (UHV) techniques. The paper explores the issue of how the real structure of the monocrystalline sample affects its cleaning procedure. The mosaic structure of a monocrystalline sample should be taken into account in the interpretation of segregation and adsorption phenomena studies carried out under UHV conditions. Some examples of the cleaning of an Fe(1 1 1) sample from sulphur and carbon impurities are presented in the paper. Cleaning may result in obtaining two different states: clean surface and clean defects or clean surface but filled defects. According to these studies, the number of adsorption sites in the defects equals approximately 50% of the number of adsorption sites on the surface.

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Keywords: Surface cleaning; Surface contamination; Segregation; Defects

1. Introduction

Before starting any adsorption or segregation studies on metal surfaces, it is necessary to prepare a clean initial surface. Typical contamination elements on metals are: oxygen, nitrogen, carbon and sulphur. The contamination degree and the concentration of contaminants depend on the chemical composition of a sample and even on the way of fixing a sample in order to study it under UHV conditions. The methods of sample cleaning are chosen individually by experimentalists, depending on the experimental conditions and needs [1–24]. There are applied heating in an oxidising or reducing atmosphere, sputtering using noble gas ions with alternative heating or heating to high temperature, followed by (rapid) cooling. Surface segregation and reactions occurring on the surface play an important role in the cleaning procedures described above.

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2. Role of the real crystal structure in the cleaning procedure

Monocrystalline samples are not ideal, because in real samples the perfect arrangement of atoms is disturbed by defects. As a result, the so-called ''mosaic structure'' is observed, which is composed of mosaic blocks, in which the arrangement of atoms is ideal. For the better understanding of segregation or adsorption phenomena, it is necessary to take into account the mosaic structure of monocrystalline samples. The space between mosaic blocks is accessible by chemisorbed atoms. The guest atoms could be localised in the defects, on the surface, or in the bulk. The localisation of guest atoms depends on the thermodynamic rules. The schematic image of the guest atoms adsorbed on the surface and in the defect of the monocrystalline sample is shown in Fig. 1.

The defects in the sample are the paths of fast diffusion (pipe diffusion [25]) of contaminants.

As a result of high temperature annealing of the sample an equilibrium state is reached between the guest atoms dissolved in the bulk, adsorbed on the surface or in the defects opened to the surface. The equilibrium state is characterised by a degree of surface coverage with contaminant atoms, θ^S (corresponding to the number of guest atoms on the surface, N^S) and by a degree of filling of the defects with guest atoms, θ^D (also corresponding to the number of guest atoms in the defects, N^D). The equilibrium state depends on the bulk concentration of contaminants (X^B) and on the kind of material characterised by the free energy of segregation, ΔG^S, which is described by the Langmuir–McLean equation [26]:

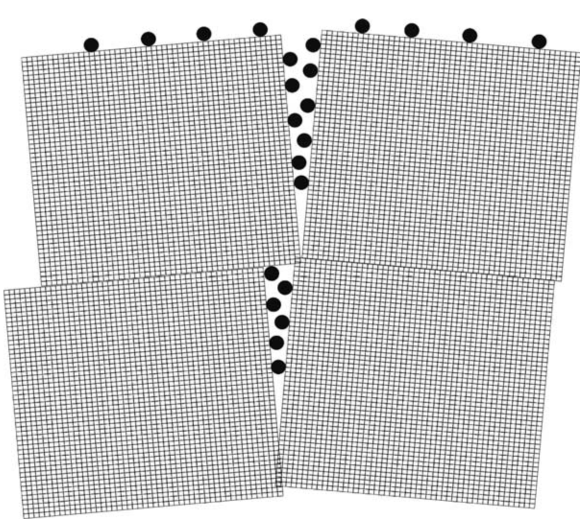

Fig. 1. Schematic representation of the localisation of guest atoms on the surface and in an opened defect of a monocrystalline sample.

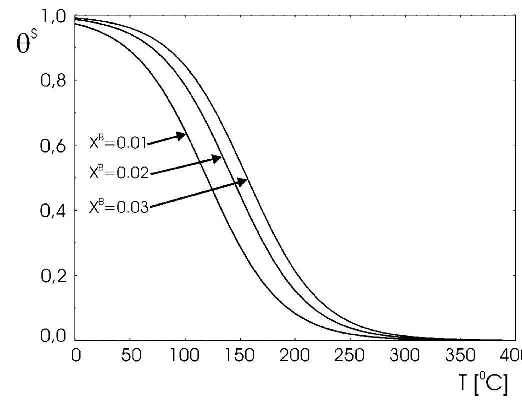

Fig. 2. Effect of temperature on the degree of surface coverage θ^S for various contaminant bulk concentrations.

$$\frac{\theta^S}{1-\theta^S} = X^B \exp\left(\frac{-\Delta G^S}{RT}\right) \tag{1}$$

Some cases of the equilibrium curves plotted according to the Langmuir–McLean equation are shown in Fig. 2. Limiting cases occur when there are no guest atoms on the surface ($\theta^S = 0$, high temperature) or, on the contrary, the surface is completely covered with guest atoms ($\theta^S = 1$, low temperature).

The Langmuir–McLean equation can be modified in order to consider the segregation from defects to the surface:

$$\frac{\theta^D}{1-\theta^D} = X^B \exp\left(\frac{-\Delta G^D}{RT}\right) \tag{2}$$

where ΔG^D is the free enthalpy of segregation from defects. Dividing Eq. (2) by Eq. (1) we obtain:

$$\frac{\theta^D}{1-\theta^D} = \frac{\theta^S}{1-\theta^S} \exp\frac{-(\Delta G^D - \Delta G^S)}{RT} \tag{3}$$

An example of the dependence between the degree of defect filling and the degree of surface coverage, plotted according to the above equation, is presented in Fig. 3.

After a long-time annealing, the homogeneity of the concentration of guest atoms in the sample has to be reached. The surface should become completely