Chapter 3

Substrate Surface Geometries and Deposits

In this chapter I will introduce the geometry of the substrate surfaces studied and also the geometry of the facet orientations that appear after alkali halide deposition on different substrates.

The substrate materials used for this work are the 3d noble metals copper (Cu) and silver (Ag). The crystal structure is face-centered cubic (fcc) with a lattice constant of $a_{0,Cu}$=3.61 Å for Cu and $a_{0,Ag}$=4.08 Å for Ag at 25 °C [Pea58]. The substrate surface orientations used are (311), (221), and (532) for Cu, and (211) for Ag. These surface orientations are vicinal to the (111) plane, i.e. they are regularly stepped or kinked surfaces with hexagonal close-packed (111) terraces.

Due to the Smoluchowski effect [Smo41] there is a charge modulation on these stepped and kinked surfaces. The electrostatic dipoles located at the steps and kinks are indicated in the side view presentations of the hard-sphere models shown below.

The experiments were performed with the ionic insulators NaCl and KCl as deposits.

3.1   Cu(211) and Ag(211)

A hard-sphere model of the (211) surface can be seen in Figure 3.1a. This surface consists of (111) terraces (three close-packed rows wide) and intrinsic (100) steps, which run parallel to the $[01\bar{1}]$ direction. The close-packed atom rows located at the step edges are characterized by a nearest-neighbor distance of 2.55 Å for Cu and of 2.89 Å for Ag, whereas the intrinsic step spacing is 6.25 Å for Cu and 7.08 Å for Ag. The surface symmetry is described by a primitive rectangular unit cell (cf. Figure 3.1a). The (111) terraces and the microfacets which represent the intrinsic (100) steps are tilted by 19.5 ° and 35.3 °, respectively, to the macroscopic (211)
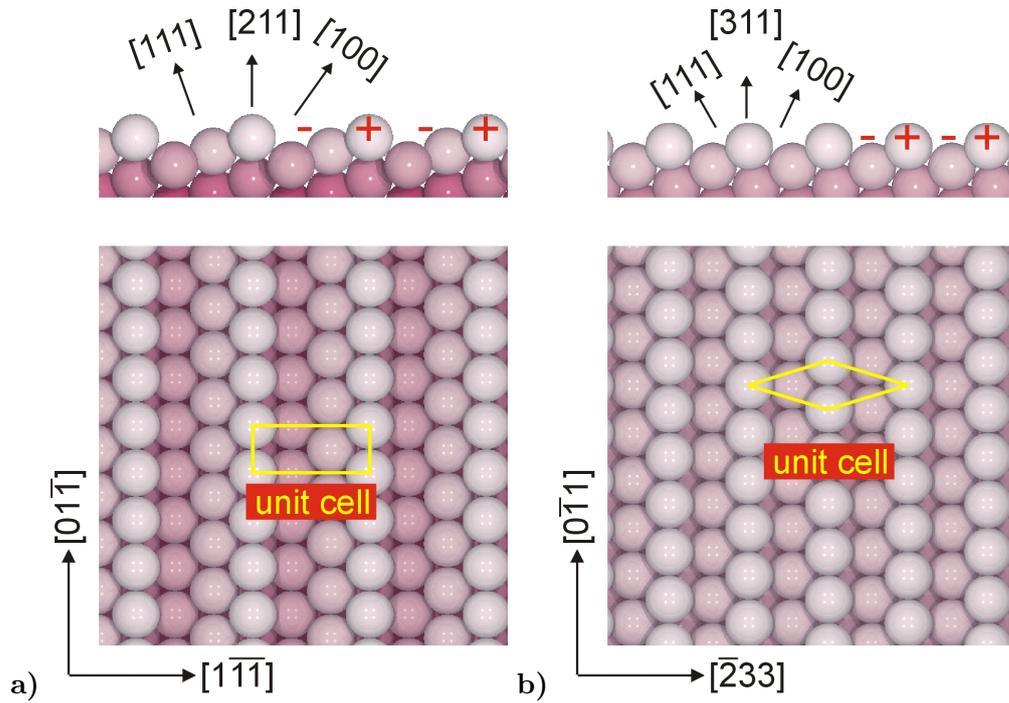
Figure 3.1: a) Hard-sphere model of the (211) surface

b) Hard-sphere model of the (311) surface

surface, which can be seen in the side view of the hard-sphere model in the upper panel of Figure 3.1a. The interlayer spacing for this surface is $0.74\,\text{Å}$ for Cu and $0.83\,\text{Å}$ for Ag.

3.2   Cu(311)

The (311) surface consists also of (111) terraces (two close-packed rows wide) and intrinsic (100) steps, which can be seen in Figure 3.1b. In this case, the close-packed rows located at the edges of the intrinsic steps are separated by $4.23\,\text{Å}$. The unit cell is represented by a rhombus with a

		Copper	Silver
Lattice constant		3.61 Å	4.08 Å
Nearest-neighbor distance		2.55 Å	2.89 Å
Separation of intrinsic steps	(311)	4.23 Å	4.78 Å
	(211)	6.25 Å [1]	7.07 Å
	(221)	7.66 Å	8.65 Å [1]

Table 3.1: Lattice spacings of the investigated vicinal Cu and Ag surfaces and facets

[1]The Cu(211) and the Ag(221) surfaces were not investigated in this work.
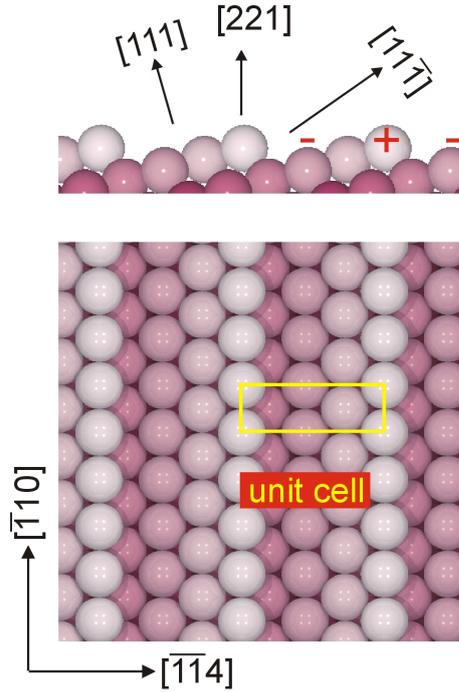
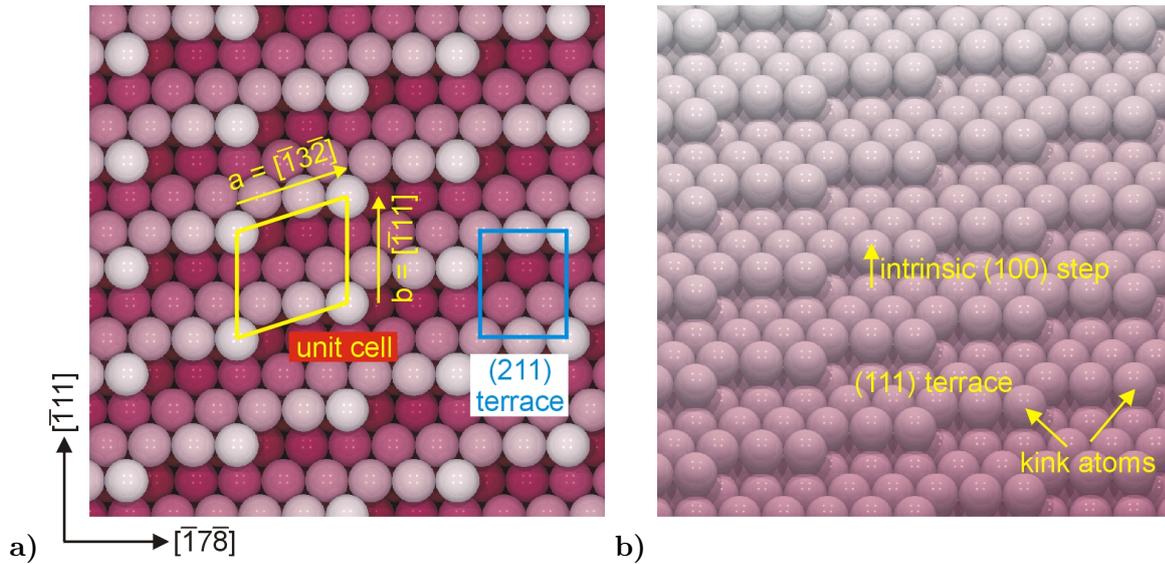**Figure 3.2:** Hard-sphere model of the (221) surface

side length of 4.42 Å and an angle of 33.6 ° and 146.4 °, respectively, between the sides.

3.3   Cu(221)

The Cu(221) (cf. hard-sphere model in Figure 3.2) is also a vicinal surface with (111) terraces (four close-packed rows wide). In comparison with the two previously described surface orientations, this surface has intrinsic (111) steps instead of (100) steps. These (111) steps run parallel to the [$\bar{1}$10] direction and have a spacing of 7.66 Å for Cu along the [$\overline{11}$4] direction. The primitive rectangular unit cell can also be seen in Figure 3.2. The side view of the surface shows that the (111) terraces are inclined by an angle of 15.8 ° and the microfacets representing the intrinsic [11$\bar{1}$] steps are inclined by an angle of 54.7 ° relative to the surface normal of the (221) surface. The interlayer spacing for the Cu(221) surface is 0.60 Å.

3.4   Cu(532)

The three surface orientations described above, (211), (311), and (221), are all stepped surfaces vicinal to the (111) plane, i.e. they have no mirror symmetry with respect to the plane which contains the surface normal and the step direction. On the other hand, there is mirror symmetry
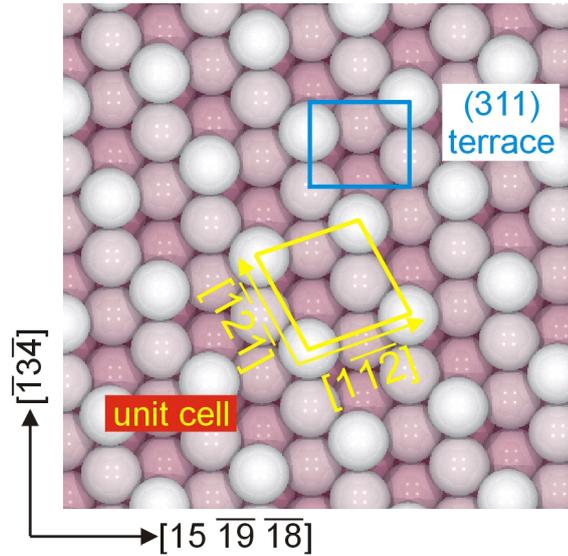
Figure 3.3: a) Hard-sphere model of the (532) surface
b) perspective view of the (532) surface

relative to the plane containing the surface normal and the direction perpendicular to the steps. The (532) surface, which is a kinked surface, has no mirror symmetry at all. Figure 3.3a displays a top view of the related surface geometry, and in Figure 3.3b a perspective view of this model is shown. Cu(532) can be described as a kinked Cu(211) surface. A (211) terrace measuring two Cu-Cu spacings along the steps and one step spacing perpendicular to the steps is indicated by the rectangle in Figure 3.3a. In the case of Cu(532), kink atoms are incorporated every two and a half Cu-Cu spacings along the intrinsic step direction. This configuration leads to a parallelogram-shaped primitive unit cell with angles of $72°$ and $108°$, and with dimensions resulting from the intrinsic step separation of $6.25\,\text{Å}$ and from the distance of the kink atoms of $6.75\,\text{Å}$ along the $[\overline{1}3\overline{2}]$ direction (Figure 3.3a). For this surface the interlayer spacing is $0.29\,\text{Å}$.

3.5   Facet Geometry: Cu(531)

To complete the geometrical description of the surfaces, the properties of the Cu(531) surface will be explained in the following. This orientation occurs as a stable facet orientation after the deposition of alkali halides on the Cu(532) surface.

The (531) surface can be described as a kinked (311) surface where kinks are incorporated after one and a half Cu-Cu spacings along the close-packed rows. A hard-sphere model with the rhombic primitive unit cell can be seen in Figure 3.4. The dimensions of the unit cell are $4.42\,\text{Å}$ and the angles enclosed measure $99.6°$ and $80.4°$, respectively.

Figure 3.4: Hard-sphere model of the (531) surface

3.6 Deposits

The investigations in this work are carried out with alkali-metal halides as deposits, which are in particular sodium chloride (NaCl) and potassium chloride (KCl).

Their prototypical rock salt structure is characterized by a sixfold coordination of each ion, i.e. each cation has six anions as nearest neighbors and vice versa (Figure 3.5). This is equivalent to a fcc crystal structure with a unit cell containing a cation and a neighboring anion. The structure of alkali halides is determined by the radii and the charges of the ions. From these quantities one can calculate the energy for the Coulomb interactions within the crystal, the so-called Madelung energy, which represents the main contribution to the binding energy of the ionic crystals [Bur82, Kit83]. A geometrical prediction of the structure of alkali halides is possible from the radius ratio ρ $(= r_+/r_-)$ of the anion r_+ and the cation r_-. Whenever the anion and the cation are of approximately the same size, the preferred structure is one wherein each ion has the largest number of oppositely charged neighbors, which occurs in the 8:8-coordinate CsCl structure. Geometrical considerations show that for $\rho < 0.732$ the rock salt (6:6) structure becomes more stable [Bur82]. The ratio of the ion radii are 0.69 for NaCl and 0.91 for KCl. This shows that this simple geometrical rule works for NaCl, but fails for KCl; and in spite of these failings it is surprising to find these rules still said to have predictive use in the crystal chemical folklore [Bur82]. For e.g. NaCl, KCl, and RbI, the rock salt structure which is a fcc structure is the observed crystal structure, whereas the alkali halides composed with cesium (CsI, CsBr, CsCl) have the eightfold CsCl structure. From theoretically calculated
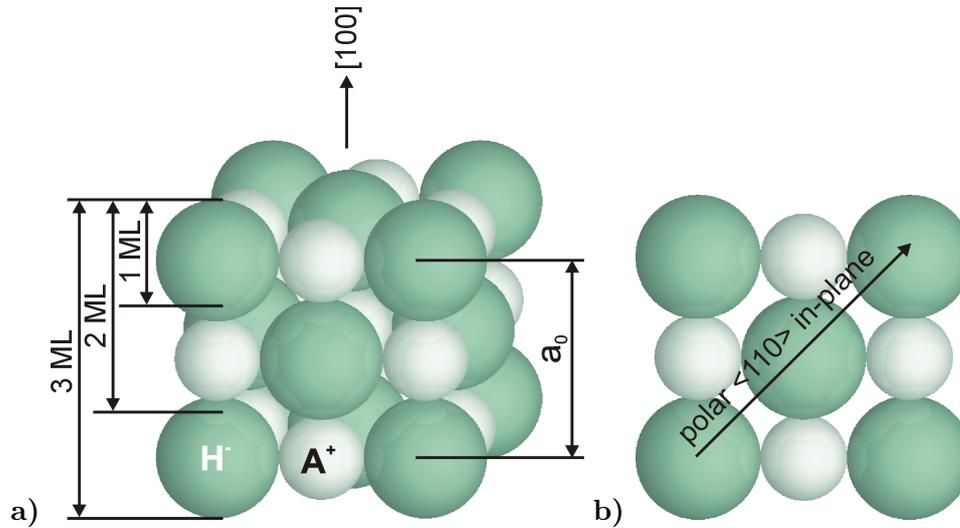
Figure 3.5: Hard-Sphere model for the rock salt structure of alkali-metal halides
a) perspective view with 3 monolayers illustrated
b) top view on a (100) oriented alkali halide layer

ion radii of these alkali metals and halogens one gets the distance between the ions [Huh88] and subsequently the lattice constants. The bulk values are 5.64 Å for NaCl and 6.29 Å for KCl [Wyc65].

The electronic bulk properties of alkali halides are described in the following. Alkali halides are ionic insulators with a wide band gap between 6.1 eV (RbI) and 13.6 eV (LiF). There have been numerous investigations with a variety of experimental techniques, like angle-resolved photoemission using synchrotron radiation [HS78], photoconductivity measurements [TH59], or ultraviolet photoelectron spectroscopy [PJLL75], which are for instance summarized in [PJLL75]. As a result, values for the band gap were derived, which amount to 8.5 eV for NaCl and 8.4 eV for KCl. Uncertainties arise from the difficulty to precisely determine the location of the band edges of the alkali halides and, because the measurements were carried out at different temperatures.

Further investigations of alkali halides were focused on structural properties, especially on the equilibrium crystal planes. Calculations of the surface energies of different orientations [Ben61, Wol92] and the equilibrium shape of the crystal [SW88] determined the (100) planes as the stable equilibrium planes for NaCl and the other fcc alkali halides, with surface free energies of ~0.2 eV per surface unit cell for the alkali halides listed in Table 3.2. These findings suggest that also thin films will preferably grow in (100) orientation, which is indeed verified in previous studies for alkali halides on metals (e.g. NaCl on Al (111) and Al (100) [HRH+99], NaCl on Cu(111) [BBB+99]), and alkali halides on semiconductors (e.g. NaCl on Ge(100) and Ge(111) [FBH89, SSP93], LiF on Ge(100) [LSEHT91], and NaCl on GaAs [SNK92]). In this work, one

Alkali halide		NaCl	KCl
Lattice constant [Wyc65]		5.64 Å	6.29 Å
Appearance		crystalline solid	
Equilibrium plane [Ben61, Wol92]		(100)	
Surface free energies [Ben61]		211 erg cm^{-2}	175 erg cm^{-2}
		1.32 eV Å^{-2}	1.09 eV Å^{-2}
Melting point [Win02]		801°C	771°C
Boiling point [Win02]		1413°C, 1465°C	1500°C
Density [Win02]		2170 kg m^{-3}	1988 kg m^{-3}
Band gap [PJLL75]		8.5 eV	8.4 eV
Ion radii [Huh88]	alkali-metal	1.16 Å	1.52 Å
	halide	1.67 Å	1.67 Å
Distance between cation and anion		2.81 Å	3.14 Å
Lattice energy [Huh88]	Born-Haber-cycle	770 KJ mol^{-1}	701 KJ mol^{-1}
	calculated	778 KJ mol^{-1}	709 KJ mol^{-1}

Table 3.2: Physical properties of NaCl and KCl

alkali halide monolayer (ML) in (100) orientation is defined as indicated in Figure 3.5a (hence, the graph shows three alkali halide monolayers in (100) orientation).

A summary of the physical and electronic properties of the alkali halides investigated is given in Table 3.2.