8. Summary

The ionic crystal calcium difluoride was investigated with ultraviolet-photoelectron spectroscopy, optical absorption spectroscopy and electron stimulated desorption.

Photoemission from ionic materials is characterized by some peculiarities that were investigated in detail. Among the investigated effects were sample charging, final state effects due to strong localization of the electronic states, the influence of phonons on photoemission and photoconductivity.

Due to the localized character of the valence band states, photoemission from CaF_2 cannot be described within the bandstructure picture like it is possible for metals. Instead, Born model binding energies were found to better describe experimental findings.

The validity of the quasidirect transition picture proposed by Himpsel and Steinmann [HSt78] was tested. It was shown that for films with thickness comparable to the electron-phonon scattering lengths, direct transitions in the photoemission spectra can be identified, while for thicker films, the original kinetic energy distribution of the photoelectrons is smeared out due to electron-phonon scattering.

During UV-irradiation of CaF_2, an increased electrical conductivity was observed which at elevated temperatures assisted in reducing the positive surface potential. The dependence of peak positions on sample temperature and UV-intensity was consistently interpreted with a model that proposed thermal detrapping of valence band holes (V_K-centers) created in photoemission. The activation energy for V_K-center motion that was determined agreed excellently with values published in literature.

The electronic structure of differently prepared CaF_2 surfaces was investigated, i.e. surfaces produced by cleavage in air and UHV, polished surfaces, and surfaces of thin films evaporated on Si(111). In the present thesis, first UPS measurements from CaF_2 crystals cleaved in UHV are shown. Impurity states on crystals that were cleaved in air and on polished crystals were investigated. Compared to crystals that were cleaved in UHV, samples cleaved in air exhibited a large density of additional states in the bandgap. By gas dosage experiments, these impurity related states could be assigned to oxygen that dissolves in the lattice. It was found impossible to remove the impurities by heating.

Changes in the electronic structure of CaF_2 were induced by electron irradiation (1.5 -2.5 keV) and photon irradiation (21.2eV).
Electron irradiation of crystals cleaved in UHV caused the fluorine valence band emission to strongly decrease, an effect attributed mainly to the reduced escape depth in the defective material and only to a minor part to fluorine desorption. In spite of the strong metallization that was observed after irradiation, no photoemission signal from Ca states in the bandgap of CaF_2 was detected, presumably due to the low cross section for excitation with 21.2 eV light.
During electron irradiation of crystals cleaved in air, the oxygen dissolved in the lattice reacts with calcium metal to form CaO, and a distinct O2p peak becomes visible in the bandgap of CaF_2. From the electron dosage dependence of the O2p yield, the oxygen concentration in the surface region of the air cleaved crystal was estimated to be 6 %.
During simultaneous oxygen dosage and UV irradiation, a chemical reaction at the surface was observed to produce CaO. In dosage experiments with films of different thickness, the oxygen signal after saturation was found to depend on film thickness. It is concluded that O^{2-} is distributed uniformly through the film. The experimental results were compared to calculations of the oxidized and OH^- covered CaF_2 surface. A reasonable agreement was found.

In this work, it was possible to observe *F*-center states with photoemission in additively colored films, but never in electron irradiated films, even not when experiments were performed at low temperature (140 K). It was however shown by optical absorption spectroscopy that *F*-centers do exist in electron irradiated bulk crystals at low temperature. The reason for the lack of *F*-center emission from electron irradiated films could so far not be determined.

Electron stimulated desorption of F^+ ions from CaF_2 was investigated using primary electron energies ranging from 0.6 to 3.0 keV.
Irradiation resulted in a positive charged sample surface, thus giving an electrostatic contribution to the positive ion desorption energies that remained undetermined in previous work. In this thesis, a method was presented which allowed for the first time to measure a positive surface potential of an insulator under electron irradiation. With this method, the dependence of the surface potential on stoichiometry was investigated. It was shown that coverage of the surface with oxygen or fluorine results in a high positive potential, while metallization causes a low surface potential. In particular, the surface potential of crystals

cleaved in UHV shows a pronounced minimum after about 10 to 20 min of electron irradiation. This effect could be explained by fast depletion of the topmost fluorine layer during the first minutes of electron irradiation, followed by an increased surface coverage with fluorine due to diffusion from the bulk. No such transient behavior was observed for crystals cleaved in air.

Utilizing the Ar^+ method, the kinetic energies of F^+ ions desorbing from CaF_2 crystals was corrected for surface charge to determine the desorption energy characteristic for the Knotek-Feibelman process. After correction, the maximum of the ion kinetic energy distribution was at about 0.9 eV for crystals cleaved in UHV. Dosage of oxygen or CO_2 during electron irradiation lowered the intrinsic kinetic energy distribution. For both gases, the charge corrected ion kinetic energy dropped by about 0.8 to 0.9 eV upon dosage. The lower kinetic energy of the particles was interpreted as an effect of the altered lattice recoil motion after adsorption.

The influence of field driven diffusion on desorption was demonstrated by comparing the ion yield from crystals and films. The yield from crystals was observed to increase after about 10 to 20 min of electron irradiation, a finding that was interpreted as due to diffusion of I-centers from the bulk to the surface in the irradiation induced field. To interpret the relative dependencies of surface potential, surface stoichiometry and ion yield, it was proposed that a high surface potential causes efficient field driven diffusion of fluorine to the surface, thus resulting in high coverage of the surface with fluorine, which in turn stabilizes a high surface potential.

Desorption from thin films showed a different temporal development than from bulk crystals. After about 15 to 30 min of electron irradiation, the ion yield from thin films exhibited a steplike increase followed by a fast decay. This steep increase was interpreted as caused by spontaneous contraction of a thin metallic film on the surface into colloids, thus exposing undamaged material to the electron beam. For a 65 nm epitaxial film, a cross section for electron stimulated desorption via the Knotek-Feibelmann process of $2.25 * 10^{-17}$ cm^2 for excitation with 1.5 keV electrons was determined from the exponential decay in the ion yield.