1. Introduction

While most of todays surface physics is focussed on semiconductors and metals, this thesis deals with the non conducting ionic crystal Calciumdifluoride (CaF_2). The material was investigated with ultraviolet photoelectron spectroscopy (UPS), optical absorption spectroscopy, and electron stimulated desorption (ESD). To my knowledge, the UPS measurements presented here are the first performed on UHV cleaved CaF_2 single crystals, in contrast to a rich literature on thin films. Also, for the first time, it was possible to determine the kinetic energy distribution of F^+ ions desorbing from CaF_2 single crystal surfaces during electron irradiation.

Calciumdifluoride is the prototype for a class of materials crystallizing in the fluorite structure. The oldest technological application of fluorite was as a raw material for the production of enamel and glasses. However, more recently the material was also shown to be useful for much more sophisticated applications. Due to its physical and chemical properties, CaF_2 is suited to fulfill a variety of technical requirements that arise in optic and optoelectronic devices. Large high purity crystals of CaF_2 can easily be grown. The material is stable in air, not hygroscopic, and does not require special handling. CaF_2 is highly transparent for light in the wavelengths interval ranging from the infrared (λ=10 µm) to the ultraviolet (UV) (λ=120 nm). It has been used for optical components both in the near UV as in the infrared for a long time [MBe75], [MFS93].

With today's high power UV laser systems, there is a growing interest in CaF_2 as a material for UV optical components [Hof92]. The most demanding application seems to arise in excimer laser systems used for laser lithography of semiconductors. Here, the width of the structures that can be produced is limited by the wavelengths of the exciting light. Presently, the 248 nm excimer laser line is used for lithography, and the corresponding optical components are made mainly of fused silica. The need to produce finer structures in the 0.25 µm range for future microelectronic devices makes it necessary to use 193 nm excimer laser light. Only few materials are suited for the transmission of these short wavelengths, like CaF_2, MgF_2 and LiF. For the production of projection optics, usually different materials are combined to compensate for spherical aberrations. CaF_2 is an excellent choice for a high refractive index material that does not exhibit any birefringence. As an additional requirement, the optical components have to withstand millions of high intensity laser pulses and this requires the use of perfectly polished surfaces meeting highest optical standards.

When conventionally polished CaF_2 surfaces are exposed to high intensity laser pulses at these short wavelengths, often the interaction of the light with the crystal has detrimental effects. As the photon energy is much smaller than the bandgap even for near UV light, absorption by electronic states generated by the polishing process plays a mayor role for the interaction process. The resistivity of the CaF_2 surface against laser damage can be greatly enhanced by applying advanced polishing techniques creating much less states in the band gap. Therefore, in this work, an attempt was made to investigate the electronic structure of differently prepared surfaces with UPS. Indeed, marked differences in the density of surface states found for polished, air cleaved, and UHV cleaved crystals are an important result of this work.

CaF_2 is also a promising candidate for the use in semiconductor-insulator structures. In today's microelectronic fabrication, insulating layers are made from amorphous SiO_2 that is produced in-situ simply by oxidizing silicon. For future three dimensional devices consisting of stacked insulator-semiconductor layers, it will be important to have crystalline insulating layers allowing a crystalline overgrowth of semiconductors. CaF_2 has been grown as a high quality epitaxial film on a variety of semiconductors that are of technological interest [DMK97], it is used in semiconductor on insulator structures (SOI), and as an improved gate insulator in three dimensional integrated circuits [SFa89], [SWS94]. It has also been shown that field effect transistors can be build with CaF_2 as insulating layer [SPA84]. Structures can be imprinted into the CaF_2 films using an electron beam metallizing the surface. The remaining calcium metal can be washed away with water [HMD82]. With this technique, structures of 2 nm width have been produced on alkali halides [IMu81].

The last step needed to reach the goal of a three dimensional microelectronic device, the overgrowth of a semiconductor on CaF_2, is much more difficult to achieve. Due to the high surface energy of semiconductors compared to insulators, there is a strong tendency of island formation and epitaxy is difficult to achieve. However, when increasing the surface energy of CaF_2 by electron irradiation, it is possible to achieve ordered layer growth of semiconductors [PMM94].

From the applications described above, it is clear that a deeper understanding of defect processes in and at the surface of CaF_2 is of great importance for both, improving the stability of CaF_2 under UV laser irradiation as well as electron beam material processing.

Early work on defects and defect generation in CaF_2 was centered on bulk processes and results were obtained mainly with electron spin resonance. Excitation energies for defect production were usually in the MeV region. A survey of the work up to the middle seventies can be found in the book of Hayes [Hay74]. More recently, scientific interest shifted to the investigation of surface and near surface damage processes. Low energy electrons ($E < 3$ keV) and UV laser light were used for defect production. Electron energy loss spectroscopy [SSA87], laser stimulated desorption and damage [EAN87], [GSJ96], optical spectroscopy [HBB98], He-scattering [LKR95] and scanning force microscopy [BRM97] were performed on pristine and defective CaF_2 surfaces.

In the first part of the present work, several surface and near surface processes are investigated in detail, using ultraviolet photoelectron spectroscopy (UPS). This method has not often been used for the investigation of insulating materials. The first ultraviolet photoemission experiment on bulk alkali halides were presented by Himpsel and Steinmann as late as 1975 [HSt75]. UPS on bulk CaF_2 samples cleaved in UHV has not been performed so far, however, a number of studies of thin films evaporated on semiconductors have been reported [OBr90]. Among these, also one example of photoemission from irradiation induced defects can be found [KHM86].

In the second part of this thesis, results for electron stimulated desorption (ESD) are presented and discussed. Many groups are active in the field of ESD from a variety of ionic materials, and the results have been reported in the proceedings of the DIET (Desorption Induced by Electronic Transitions) conferences [BJS93], [SPo95], [WPa97]. Electron stimulated desorption from CaF_2 was treated both experimentally [MSS91], [ZGT94], [Rei95] and theoretically [AWa89], [CJe95], [CSo95]. Experimental work suggested that F^+ desorption from CaF_2 under irradiation is due to an inter atomic Auger process, commonly referred to as the Knotek-Feibelman process [KFe79]. Concerning the kinetic energy distribution of the desorbing particles there are partially conflicting results. In contrast to the experimental results, theoretical work denied the possibility of F^+ desorption via the Knotek-Feibelman process from CaF_2.

This thesis is organized as follows: The bulk and surface structures as well as important properties of calciumdifluoride are introduced in Chapter 2. Effects of electron irradiation are described, and point defects as the primary excitations under irradiation are presented.

The technique of photoemission is introduced in Chapter 3. It consists of a general part explaining setup and a basic theory of photoemission. The experimental apparatus used here is described in Chapter 4.

Chapter 5 presents the photoemission results. The chapter starts with a survey of general features of photoemission from CaF_2, followed by a more detailed discussion of deviations from the direct transition picture of photoemission, and the conduction mechanism under UV irradiation. In the second part of Chapter 5, photoemission results from differently prepared CaF_2 surfaces are compared with each other. This allows the characterization of bandgap states from crystals cleaved in UHV and in air, polished crystals, and thin epitaxial films. These studies are complemented by an investigation of changes in surface electronic structure due to a controlled dosage of surfaces with gases. The third part of the UPS chapter deals with irradiation induced effects in CaF_2 and it is demonstrated how electron and photon irradiation changes the electronic structure.

Chapter 6 contains a short optical absorption study on electron irradiated CaF_2 crystals to show that isolated *F*-centers can be produced by low energy electron irradiation at a temperature of 150 K.

Electron stimulated desorption is the subject of Chapter 7. A new method that allows to determine the magnitude of the positive surface potential under low energy electron irradiation was invented. The temporal evolution of surface charge during irradiation and the influence of surface stoichiometry on the surface potential was investigated. With the help of the method for surface potential determination, the charge corrected kinetic energies of F^+ ions desorbing from CaF_2 crystal surfaces could be obtained for the first time. It is shown that the kinetic energy of desorbing F^+ ions changes upon adsorption of oxygen and CO_2 during irradiation. Furthermore, desorption from air and UHV cleaved crystals and thin epitaxial films is compared.