Surface Modification of CaF_2

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A brief overview of the techniques used in thin film growth, analysis and modification, followed by an explanation of CaF_2 structure. Electron irradiation and As termination are discussed with regards to CaF_2 and the question of As interaction is addressed.

INTRODUCTION

This summer, I work in Marjorie Olmstead's condensed matter lab. The focus is on epitaxial growth of various crystalline solids on silicon substrates. Among these crystals is calcium floride, which will be the focus of this paper.

BACKGROUND

Molecular Beam Epitaxy

The technique we use to grow thin film is called Molecular Beam Epitaxy (MBE). The process involves an evaporation cell which consist of a heating filament wrapped around a crucible. The crucible is filled with the desired growth material, in this case CaF_2, and then placed on an Ultra High Vacuum (UHV) chamber with a base pressure of 10^{-10} torr. As the cell is heated, the growth material is evaporated into the chamber, and deposited onto the substrate. This process allows for relatively well controlled growth, with four major parameters available for adjustment. These parameters are cell temperature, which controls the flux, the substrate temperature, which can be changed to promote nucleation, the substrate itself and finally the total growth time. Using MBE allows for consistent growth of CaF_2 films on the Si (111) substrate.

Apparatus

As was mentioned above, the environment in which all of our experiment with CaF_2 take place is in a UHV chamber, with a base pressure of 10^{-10} torr. Such a low pressure is necessary to insure that no undesired compounds are deposited on the substrate, either during growth or during analysis. A schematic of the dual chambers used can be seen in Fig 1,

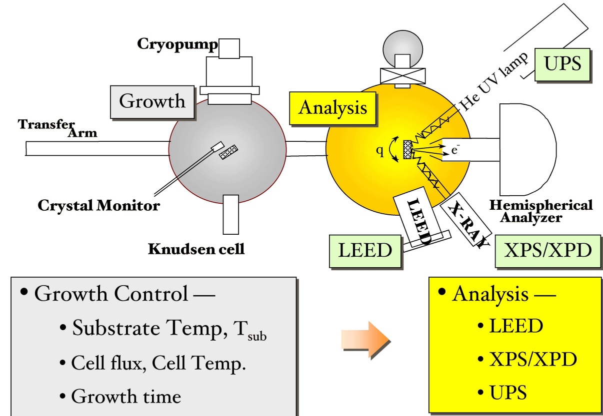

FIG. 1: Schematic of the dual chambers used showing both the growth and analysis chambers. Also shown are some of the analysis techniques including XSP.

X-Ray Photo-Electron Spectroscopy

A common data acquisition technique we used is called X-Ray Photo-electron Spectroscopy, or XPS. The basic idea is x-ray photons of a constant energy are shot at the sample, and excite electrons in the crystal. If enough energy is transferred to the electrons, they can escape the crystal with a kinetic energy given by

$$KE(e^-) = h\nu - BE - \phi \tag{1}$$

where $h\nu$ is the incident photon energy, BE is the binding energy associated with the electron's initial state, and ϕ is the value of the inner potential barrier found at the crystal surface. The kinetic energies are scanned with a hemispherical analyzer, and the spectrum produced is characteristic of the elements present. XPS is relatively sensitive to chemical environments and thus shifts in expected peaks can be used determine the composition of interface, bulk and surface elements of thin films.

CALCIUM FLORIDE

Calcium Floride (CaF_2) is an ionic crystal insulator that happens to have a very good lattice mismatch with the Si(111) surface. This brings up intriguing possibilities

for Si/CaF_2/Si layering, and possibly the development of three dimensional circuitry. While the growth of CaF_2 on Si(111) is relatively well understood[1][2], the attempts to grow Si on CaF_2 run into a variety of different problems.

The CaF_2/Si interface has a growth temperature dependence, with stable, type B interfaces forming only at temperature of above 600° C. In this temperature range, the preferred bonding arrangement is a F-Ca-Si, the the second F^{1-} ion having been removed from the interface layer. Subsequent layers are deposited only after a complete interface has been formed. These bulk layers are in the conventional CaF_2 structure, Ca^{2+} ion located in an fcc lattice, with F^{1-} occupying the tetrahedral holes.

Because CaF_2 is an ionic crystal, it has no surface reconstruction. The top layer formed in growth is a F^{1-} mono-layer, which has a strong interaction with Si. It is this interaction, along with the much higher surface energy of Si ($\sigma(\text{Si}) = 300\%\sigma(\text{CaF}_2)$), that prevents the laminar growth of Si on CaF_2. The removal of this top F^{1-} layer would not only reduce the Si-F interaction, but it would also increase the surface energy of the CaF_2 film.

ELECTRON STIMULATED DESORPTION

The process with which we remove the F^{1-} ions was first explained by Knotek and Feibelmen in 1978[3], although it was not the process that was occurring in the various oxides that they studied at the time. It has since been shown that CaF_2 is one of the few systems for which this theory applies. The basic model involves a low energy electron excitation of a hole in the Ca 3p band. Since this is the highest energy level in the Ca^{2+}, an inter-atomic Auger electron decay takes place, with an electron from the F 2p decaying into the hole, and transferring the energy loss to another electron in the same band. This Auger electron is then expelled from the F ion, which, with the loss of two electrons, has a positive charge. The F^{1+} is then expelled from the crystal by Coulomb expulsion.

While electron irradiation of the kind has been shown to be a effective and controllable method for F removal[1], it changes the surface of the CaF_2 to one of highly reactive Ca metal. This surface, even in UHV conditions, rapidly becomes oxidize, as can be seen in Fig 2. In order to passivate irradiated surfaces, they are exposed to As, as is discussed below.

ARSENIC PASSIVATION

From past research, we know that As works to passivate the surface, and that As will only bond to irradiated CaF_2[1]. It also has the added benefit of acting as a surfactant for Si growth, although only if it is located at the surface. Data, taken on thick film (40Å)

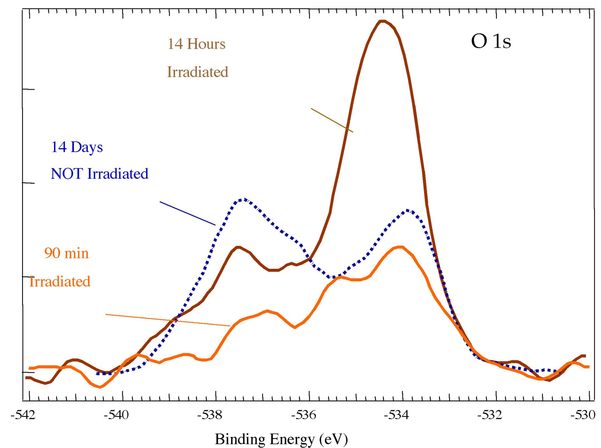

FIG. 2: XPS spectra of the Oxygen 1s energy level, comparing irradiated and non-irradiated CaF_2 for different exposure times in UHV conditions (base pressure of 10^{-10} torr)

CaF_2 samples that were irradiated at room temperature in the presence of As and then annealed in As, showed approximately 1/3 of a mono-layer of As (compared to As:Si(111) mono-layer measurements). However it was unclear if this As was located at the surface, or if, during the annealing process, the As had diffused through the bulk to the interface layer, where attenuation of the peak would produce similar results.

Experiments were done to attempt to resolve this issue, the data for which can be found in Fig 3. Two samples were grown, both thin films, approximately 4-5 layers of CaF_2. The first sample was irradiated in an As background of 10^{-8} torr at room temperature, then annealed to 550°C in UHV conditions. A As 3d XPS spectrum was taken in between each of the steps. The second sample was treated as past, thick films had been, with both irradiating and annealing in As before a spectrum was taken.

As is shown in Fig 3, the non-annealed sample shows substantially more As then the same sample post annealing. This indicates that the As is probably deposited on the surface and diffuses into or through the bulk CaF_2 with annealing. The shift in binding energy of the non-annealed peak is thought to be due to a strong dipole from the As_4 tetrad, the preferred structure of As at room temperature, which is the most likely form the As is in on the surface. The shift is removed upon annealing, because the tetrad is broken by the time temperatures of 550°C are reached.

The full mono-layer that is presents in the second sample is of a different nature than that discussed above. It is most likely at the interface or diffused through out the bulk. The peak has not been shifted in energy because the annealing process has again broken the tetrad structure, and it's intensity can be accounted for by the thinness of the film itself. Unlike the thick films studied

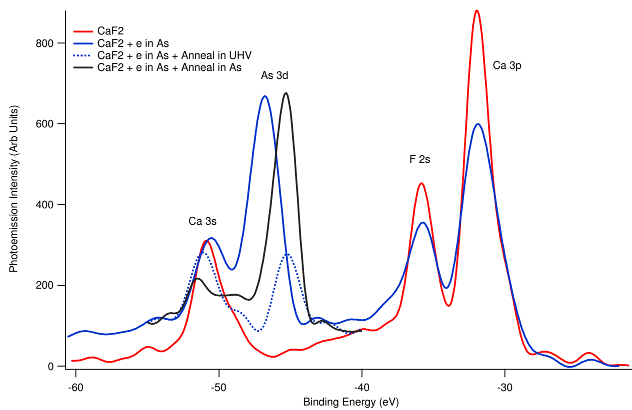

FIG. 3: XSP data taken of the As 3d peak during various stages growth, irradiation and annealing, as labeled.

perviously, the attenuation of the interface is relatively small.

CONCLUSION

Using basic surface growth and analysis techniques, such as MBE and XPS, we are able to consistently grow CaF_2 films on Si(111). Electron Irradiation both removes the surface layer of F^{1-} ions and increases the surface energy of these films, which should promote the subsequent growth of Si. However, it also greatly increases the reactivity of the surface. To reduce this effect, films are irradiated in the presence of As, which acts as both a passivate for the film and as a surfactant for Si. The question of the effect of annealing on the As surface layer is as of yet unresolved, but it appears that it allows the As to diffuse into the bulk, possibly even down to the interface layer. Experiments have been planned to use Antimony instead of As, because of Sb similar chemical reactions and its greater size. The hope is that the increase in size will prevent the Sb from diffusing down.

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[2] E. Rotenberg, *The relationship between structure and core-level shifts in thin epitaxial films of caf$_2$ and srf$_2$ on si(111)* (1993).

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