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# Ion beam irradiation of thin $CaF_2$ films: A study of lithographic properties

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The technological track to ever smaller devices in very and ultra high scale integration schemes with feature sizes lower than 1 μm, carries classical photolithographic methods to physical limits, and is claiming a transition to lower wavelength or particle irradiation. New resist materials and exposure techniques are under study. Earth Alkaline Fluorides, such as $CaF_2$, $BaF_2$ and $SrF_3$, decompose under electron and ion irradiation by desorbing Fluor, and oxidizing the remaining earth alkaline metal under the presence of Oxygen. The solubility of the oxidized areas is then modified. The present paper deals with resist properties of $CaF_2$ under ion beam exposition with $Ar^+$-, $He^+$-, $Si^+$-, and $O^+$-ions. RBS measurements are applied in order to determine modifications in the film composition. Positive and negative resist behavior is found in water and dilute HCl, respectively. Both, the change of chemical composition and the pattern characteristics correlate with the energy deposition of implanted ions. Characteristic lithographic curves are shown.

## 1. Introduction

The study of lithographic properties of calcium fluoride ($CaF_2$) thin films is interesting for at least two reasons: On the one hand, $CaF_2$ grows epitaxially on silicon wafers. The lattice misfit between the two cubic crystal structures at room temperature is with 0.6% quite small and guarantees under appropriate growth conditions a high quality crystalline heterosystem [1-3]. In addition the dielectric constant of $CaF_2$ is with $\varepsilon = 6.9$ almost twice as high as that of $SiO_2$, which makes it an interesting material in memory devices [4]. From a theoretical viewpoint, silicon on insulator (SOI) is the most attractive technology for low-voltage ULSI circuits [5]. A thoroughly epitaxial pile up of silicon-insulator-metal layers makes a three-dimensional microelectronics integration feasable.

On the other hand, as device sizes shrink, some point must eventually be reached when common transistor structures cannot be made any smaller and new device concepts have to be introduced. Meanwhile the high integration level of the actual microelectronics is reached by permanently reducing the lateral feature sizes far below the one micrometre scale. Photolithography is hitting physical limits, and the incorporation of other than light-optical methods beyond the 0.35 μm technology becomes demanding.

The application of fine particle beams as structure-forming tools makes new resist materials indispensable. It is known from earth alkaline fluorides (EAF), that the interaction with energetic electrons causes desorption of fluor. The presence of oxygen within the reaction chamber, where an electron beam hit the surface of, say, $CaF_2$ will then result in the formation of CaO. Vapor pressure and solubility of these two materials are quite different. One of the mayor limitations of the direct irradiation process with energetic electrons, however, is the large exposure dose of between one and ten Coulombs per squared centimeter.

Supposing that the energy deposition of energetic particles into the $CaF_2$ -film is an essential aspect for a successful lithographic process, the application of energetic ions instead of electrons should provide then for a reduction of the necessary exposure dose to more comfortable values. It is the aim of the present paper to study lithographic properties of $CaF_2$ under the impact of an energetic ion beam of different ion mass and acceleration energy. Different chemical solutions are considered in order to produce a lithographic effect of the illuminated films.

## 2. Experiments

Polycrystalline $CaF_2$ -films on silicon wafers are produced by thermal evaporation of $CaF_2$ at a base pressure of $10^{-4}$ Pa. This approach is dictated by the high number of samples needed during the course of this study. Samples grown by MBE will be used in future experiment.

The $CaF_2$-films were grown 75...100 nm thick with a growth rate of 1.5 nm/s. Ion beam irradiation of the samples was carried out in a $10^{-4}$ Pa base pressure implantation equipment, using $He^+$-, $Ar^+$-, or $Si^+$-ions with 60 keV acceleration energy, as well as $O^+$- ions with 30 keV energy. RBS was applied in order to probe the chemical composition of the thin films, using 1.7 MeV $He^+$-ions.

The beam diametre was 1 mm, and the measuring dose 10 μC, which corresponds to a very low “exposure dose” of $6.10^{15}$ $cm^{-2}$. RHEED images were taken from the irradiated films, and modifications of the (poly) crystalline structure detected. In order to produce a selective dissolution behavior between irradiated and non-irradiated regions on the film, two different solutions were applied (i) distilled water, and (ii) $HCl{:}H_2O = 1{:}100$.

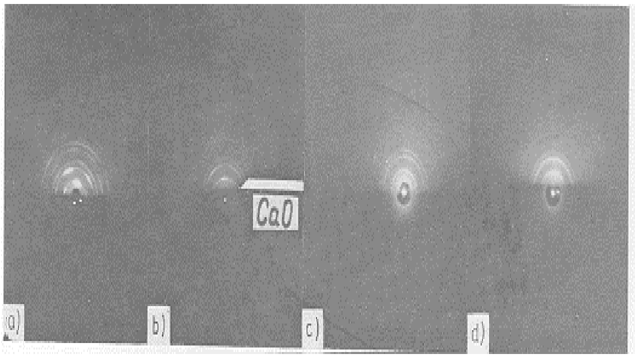

Fig. 1: RHEED images of $CaF_2$-layers, irradiated with 60 keV $Ar^+$-ions of different dose (a-0; b-$10^{16}$ $cm^{-2}$; c-3 x $10^{16}$ $cm^{-2}$; d-$10^{17}$ cm-$^{-2}$).

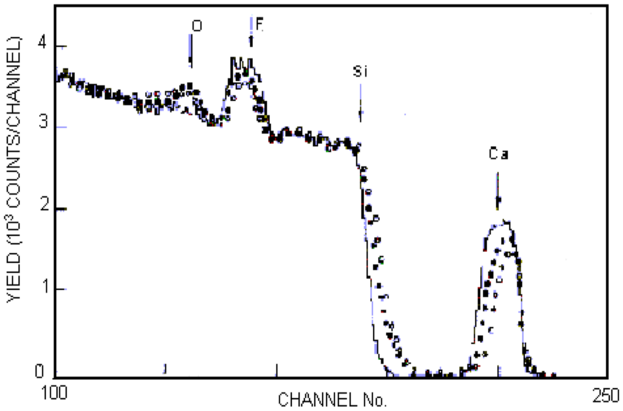

Fig. 2.: RBS-spectrum of a 100 nm $CaF_2$ -film after irradiation with 60 keV $Ar^+$-ions (circles: dose 3 x $10^{16}$ $cm^{-2}$; full circles: doses 1 x $10^{17}$ $cm^{-2}$; smooth curve: without irradiation).

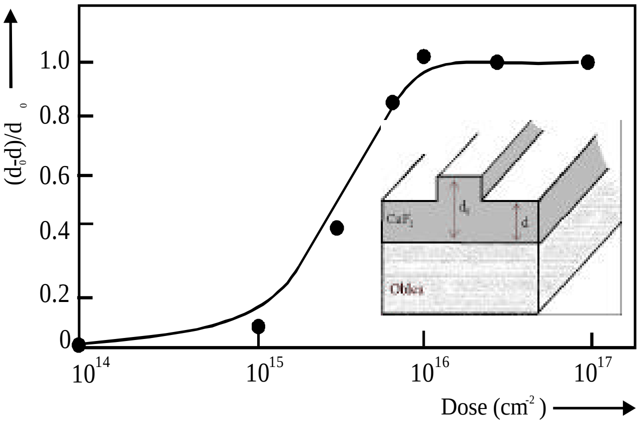

Fig. 3: Characteristic curve of a $CaF_2$ sample after irradiation with 60 keV $Ar^+$.

## 3. Results

Texture appears on the as-deposited $CaF_2$-films as seen in the RHEED image of fig. 1a. With increasing ion dose of $Ar^+$ -ions, this texture disappears. At the highest value ($10^{17}$ $cm^{-2}$, fig. 1d) diffuse reflexes indicate amorphized regions. An additional reflex of CaO is also present.

The RBS-spectrum after irradiation of $CaF_2$ with 60 keV $Ar^+$-ions is shown in Fig. 2. The effect of 60 keV $Si^+$-ions is comparable to the $Ar^+$-ion behavior, while the $He^+$ implantation does not allow a clear interpretation. The following outcome was found: Increasing ion doses lead to a $CaF_2$ sputtering seen in the reduction of the Ca -peak, and a shift of the Silicon edge; further to reduced desorption of F compared to that of Ca; as well as to increased Oxygen presence in the film, where the broadening of this peak corresponds to an increased depth in the film.

An ion-stimulated layer mixing at the $CaF_2$/Si -interface is seen in Fig 2, where the two facing edges of the Si and Ca -peak become less abrupt with increasing ion dosis. This is due to the fact that at high dosis values, the $Ar^+$-ions sputter off more of the film thickness and reach the interface, where a recoil implantation of Ca takes place. Ar and Ca possess nearly the same atomic weight, which results in a maximum energy transfer when $Ar^+$ hits the Ca.

Experimental results of the solubility of exposed films are in agreement with calculations. All irradiated films display a higher solubility in destilled water, corresponding to the behavior of a positive resist [6].

The solubility of exposed films in a solution of HCl and water, $HCl:H_2O$ = 1:100, shows an opposite behavior, -the unexposed films went into solution faster, which corresponds to a negative resist behavior. Characteristic curves are shown in Fig. 3.

## 4. Conclusions

A characteristic curve is shown in Fig. 3. No significant differences are found between 60 keV $Ar^+$-, 30 keV $O^+$- and 60 keV $Si^+$-ion irradiation. In any case dosis values around 3 x $10^{16}$ $cm^{-2}$ are sufficient to produce resist behavior. This is four orders of magnitude less than needed with electron irradiation. In the case of 60 keV $He^+$-ions the required dosis is about 1 x $10^{17}$ $cm^{-2}$, which is due to the smaller amount of energy deposition with $He^+$ ions.

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