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AFM Characterization of insulating CaF_2 Layers on a Si Wafer

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Abstract
Atomic Force Microscopy (AFM) has been used in order to characterize the surface topography of insulating CaF_2 layers. CaF_2 thin films were deposited on Si (111) substrates by means of thermal evaporation. The Si substrates were chemically cleaned prior to insertion into the system. The final volatile oxide was desorbed in situ by heating to 850°C. CaF_2 was evaporated from a Knudsen –type cell by used of a graphite crucible, while the growth temperature was held at 650 °C. Electrical properties are measured by use of a special MIS structure.

Key words: AFM, Dielectric fluoride films, thin films

Introduction

Attention to study A_{II} - Fluoride insulators was attracted by a number of potential uses, including the electron beam stimulated decomposition for creating an inorganic resist, and new electronic devices due to the single crystalline character of such a thin-film system [1-6].

During previous years Si-MBE has become an attractive tool for the realization of high quality epitaxial layers, which are difficult, if not impossible, to obtain by use of the more classical growth techniques. Heteroepitaxial growth of dielectric films on Si substrates is of considerable interest in the formation of SOI (silicon-on-insulator) structures and 3D-integrated circuits for microelectronics applications [7].

A variety of reasons makes alkaline earth fluorides, as e.g. CaF_2, a good candidate to be grown epitaxially on some semiconductors. CaF_2 crystallizes in the cubic fluorite crystal structure, which is closely related to the diamond structure of Si. The lattice mismatch is only 0.6% at room temperature. Fluorides sublime as molecules, making the problem to control film stoichiometry easy.

The use of a double heteroepitaxial growth suggests the possibility that insulator and silicon layers could be grown on silicon substrates. These heteroepitaxial structures have advantages in that a large-area SOI structure is easily attained on the full surface of the silicon substrate. In this paper, a report on results in the study of thermally deposited CaF_2 on single crystal Si substrates is given. AFM studies are carried out in order to observe the surface morphology,

1 Growth and Properties of CaF_2 Films on Si

Thin film insulators have a number of potential applications in the semiconductor industry. Two classes of insulating materials have been shown to grow epitaxially on Si when deposited by MBE, alkaline earth fluorides (CaF_2, SrF_2, and BaF_2 and mixtures thereof) and lanthanide trifluorides (e.g., LaF_3). The CaF_2/Si system has received particular attention because of the compatible crystal structures and small lattice constant mismatch (0.6% at room temperature) of the two materials. With a band gap of approximately 12 eV, CaF_2 is an excellent insulator. Its relatively large dielectric constant of 6.8 also makes it attractive for a gate insulator. Some physical properties of CaF_2 are summarized in Table 1.
It has been known that the growth of good quality films of CaF_2 on Si can be accomplished more easily on (111) oriented substrates. Ishiwara and Asano [8] found a wide temperature

range over which high quality epitaxial CaF_2 could be grown on Si (111). Besides it is difficult to obtain smooth surfaces with other crystal orientations, particularly with the (100) surface, due to their much higher free surface energies.

The CaF_2 films were thermally deposited on Si (111) substrates. In the vacuum chamber a base pressure of $1x10^{-5}$ Pa is established. The CaF_2 was evaporated from a Knudsen-type cell with a graphite crucible operated at about 1100 °C.

Table 1. Physical properties of CaF_2 bulk material

Molecular weight	78.08
Density	3,18 g/cm^3
Melting point	5870 m/s
Sound velocity	1423 ºC
Vapour pressure at T=700 K	6×10^{-18} Pa
Lattice constant at room temperature	0.5464 nm
Next atomic neighbor distance	0.236 nm
Crystal structure	cubic fluorite
Lattice misfit to silicon	+0.6% at RT
Linear expansion coefficient (at 200 K)	18.2×10^{-6} /K
Band gap energy	12.2 eV
Dielectric constant	6.8
Electrical bulk resistivity at RT	10^{13} Ohm x cm
Solubility in water at RT	1.6×10^{-5} g/cm^3

Prior to the introduction into the vacuum chamber the substrate was chemically cleaned. The wafer was loaded into the vacuum vessel and heated to remove the volatile oxide and impurities on it.

RHEED (reflection high energy electron diffraction) measurements allow to monitor the substrate cleaning. During film deposition the temperature of the substrate was kept at 650°C to 700°C. Samples with various CaF_2 film thicknesses (30-200 nm) were prepared. Atomic Force Microscopy (AFM) was used to study the morphology of the films.

2 Atomic Force Microscopy of CaF_2 thin film surfaces

The following figures 1 and 2 show characteristics of the CaF_2 surfaces on a relatively small length scale of a few squared micrometers.

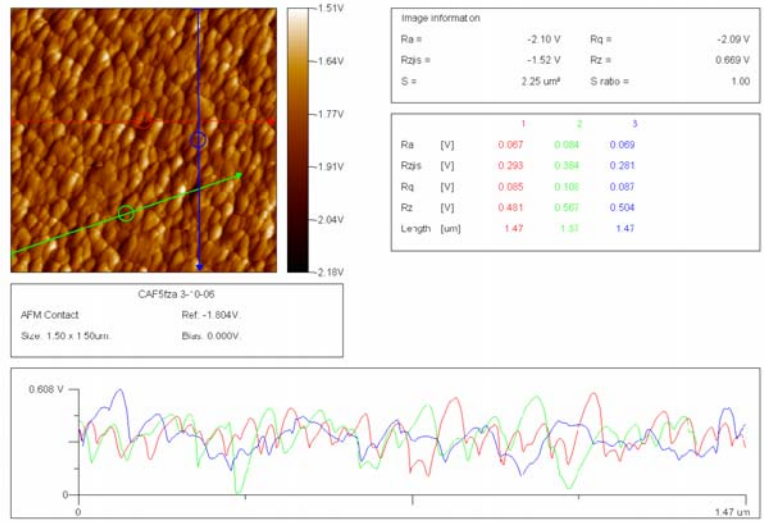

Fig. 1(a): AFM image information of a CaF_2 film formed at relatively low evaporation rate

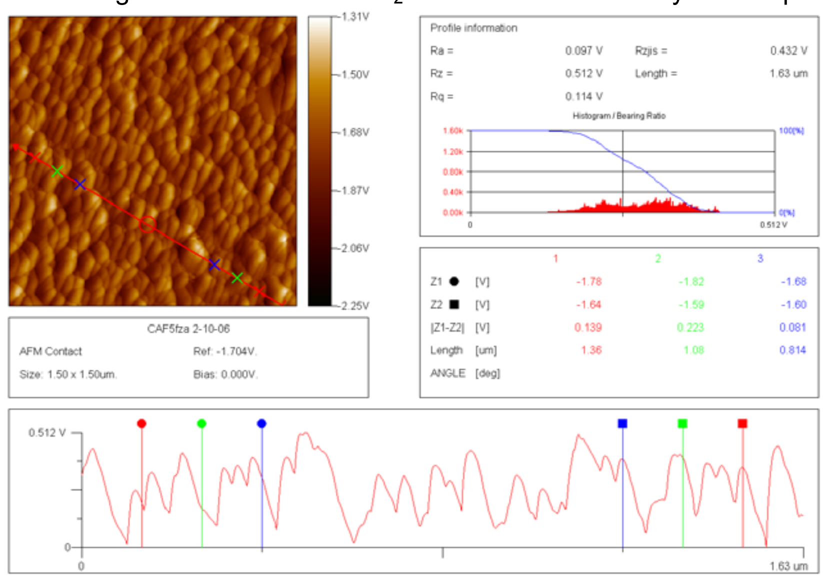

Fig. 1(b): AFM surface profile information of a CaF_2 film formed at relatively low evaporation rate

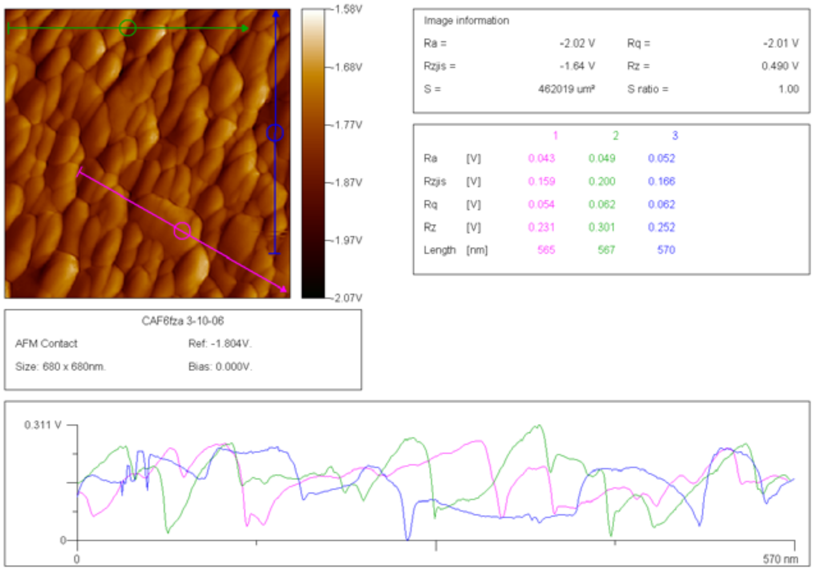

Fig. 1(c): AFM image information of a CaF_2 film formed at relatively high evaporation rate

It turns out, that the surface topography even in a small square of 2x2 [μm^2] shows characteristic structures, which are related mainly with the temperature regime during CaF_2 evaporation on the heated substrate, as well as with the molecular flux density of the CaF_2 vapour.

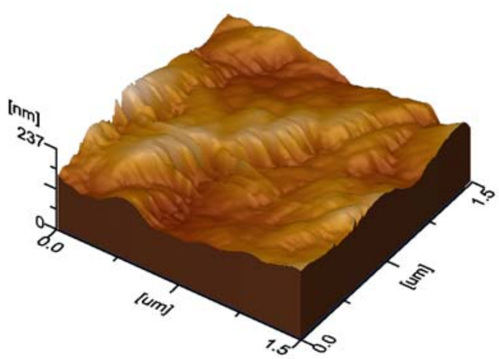

Fig. 2(a): AFM surface topography of a CaF_2 film formed at relatively high evaporation rate

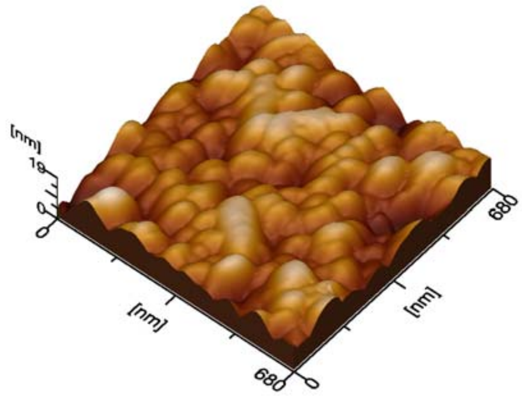

Fig. 2(b): AFM surface topography of a CaF_2 film formed at a medium high evaporation rate

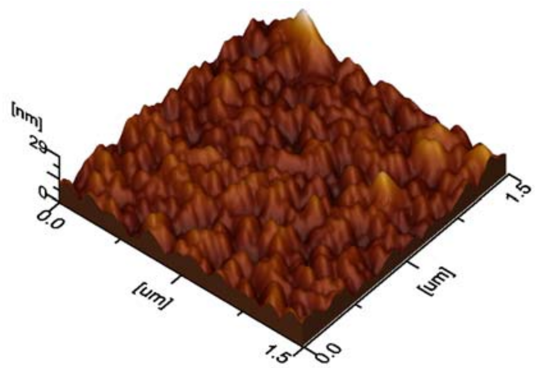

Fig. 2(c): AFM surface topography of a CaF_2 film formed at relatively low evaporation rate

3 Electrical Properties

The determination of the room temperature electrical resistivity of thin films is usually an involved problem, particularly if the substrate is conductive and the layer insulating. The electrical bulk resistivity of CaF_2 of the order of 10^{13} Ω cm (see Table1). In the present case, MIS devices are prepared by evaporating aluminum through a shadow mask onto the CaF_2 layer. The Al dot contacts of 10^{-5} cm^2 in size were applied as electrodes (Figure 4). The p^+ -n wafer structure was chosen in order to produce a reversible current break-through. This, of course, has to be distinguished from the destructive permanent breakdown of a dielectric layer. The room temperature break-through voltage in the present MIS structures is about U_s = 5.6 V. A low-impedance state is reached at a holding voltage U_H = 3.4 V. The switching and holding currents are in the microampere range. Resistance ratios of $10^2 \ldots 10^3$ for the on-off impedance are easily obtained. Taken the CaF_2 film thickness, and (reversible) break-through voltage, a dielectric strength in the order of 1 MV/cm is measured. The mechanism for the relatively large current transport though the CaF_2 layer is not well understood yet.

Given the large energy gap, the discontinuity between the conduction band between CaF_2 and Si or Al is 2.2 eV or greater [12]. Such a barrier is not easy to overcome for the charge carriers, at least if not a multi-jump process is considered. Conduction through “hot” microchannels after breakthrough is a further possibility to be considered. One of the attractive features of epitaxial insulators is the possibility of correlating electrical properties with the molecular structure of the interface.

4 MIS Device Structure

SOI structures based on Si overgrowth of heteroepitaxial CaF_2/Si structures have been prepared by several groups and provide the basis for prototype SOI device structure [2]
MOSFETS on Si/CaF_2/Si structure have recently been prepared by two Japanese groups [9-11]. Transistors have been successfully fabricated on the SOI wafers with an improved Si gate CMOS process that prevent crystal degradation during the transistor fabrication process as much as possible.

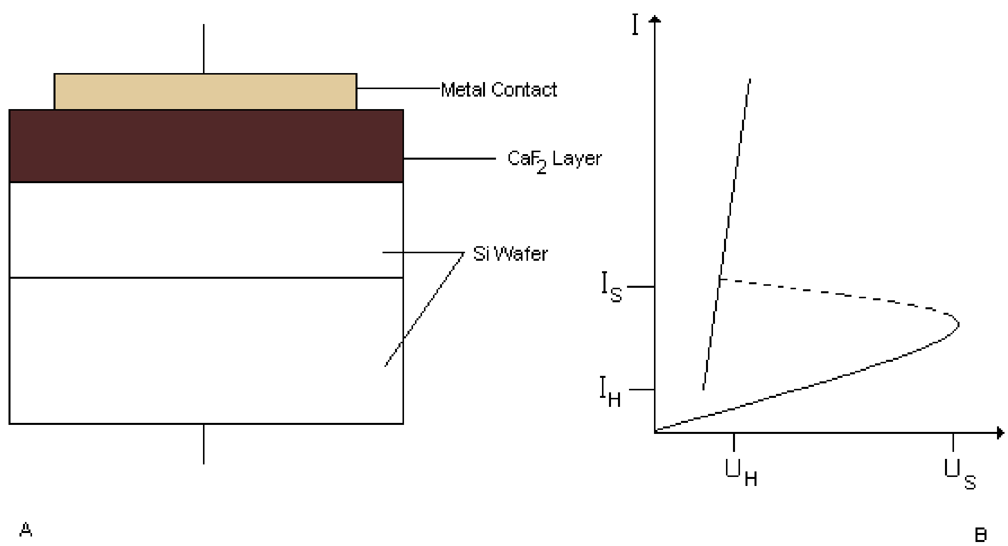

Figura 4. MIS structure (A) and typical I-U characteristics (B). Aluminum contacts are placed on top of the CaF_2 layer, deposited on a Silicon wafer. The p^+-n Si structure provides for a switching behavior of the MIS device. U_H, U_S-holding and switching voltage, I_H, I_S-correspondingly. The n-type side of the Si wafer is a 7 µm thick epi layer with an electrical resistance of ρ = 3 Ωcm.

5 Conclusions

Insulators that can be grown on Si, especially CaF_2 as a group II-fluoride, are interesting from the standpoint of both fundamental research and possible technological applications [13]. The alkaline ftuorides, exemplified by CaF_2, exhibit adequate dielectric properties to be useful as gate dielectrics. CaF_2 has also been employed as the insulating layer in SOI structures. Three-dimensional device structures are an attractive application of epitaxial ftuorides. Several kinds of epitaxial multilayer structures of metal silicides, insulators and semiconductors have recently been demonstrated.

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References

[1] Cho, C. C. , H. Y. Liu, B. E. Gnade, T. S. Kim, and Y. Nishioka: *J. Vac. Sci. Technol.* AI0, 769 (1992)

[2] Cristoloveanu, S.: *J. Microelect. Engin.* 39, 145 (1997).
[3] Phillips, J.M., and J. M. Gibson: *Mat. Res. Soc. Symp. Proc.* 25, 381 (1984) and references therein.
[4] Sokolov, N.S., J. C. Alvarez, S. V. Gastev, Yu. V. Shusterman, I. Takahashi, Iyoh, Y., J. Harada and R. M. Overney: *J. Cryst. Growth* 169, 40 (1996).
[5] Manasevit, H.M., and W. I. Simpson: *J. Appl. Phys.* 35, 1349 (1964).
[6] Ramírez, A.: Tesis Doctoral, Universidad Autónoma de Puebla, Mx. (1998)
[7] Zehe, A. , A. Thomas "Tecnología Epitaxial de Silicio" ed. ivc Dresden 2000
[8] Ishiwara, H. and T. Asano: *Appl. Phys. Lett*. 40, 66 (1982)
[9] Onoda, H., M. Sasaki , T. Katoh, and N. Hirashita: *IEEE Trans. Electron. Devices* ED-34, 2280 (1987)
[10] Asano, T., Y. Kuriyama, and H. Ishiwara*: Electronics Lett*. 21, 386 (1985)
[11] Zehe, A., in*: Cryst. Growth and Charact. of Adv. Mat.* (Ed. Christensen et al.), World Sci. Publ. Co., Singapore (1988)
[12] Johansen, H., S. Gogoll, E. Stenzel, and M. Reichling*: phys. stat. sol.* (a) 150, 623 (1995)
[13] Zehe, A.: "Moletrónica" www.moletronica.ece.buap.mx (2003)