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Characterization of Epitaxial Calcium Fluoride as a Dielectric Material for Ultra-thin Barrier Layers in Silicon Microelectronics

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Abstract

A detailed characterization of injection properties of epitaxial tunnel-thin calcium fluoride layers is performed. Electrical and optical behavior of Au/CaF_2/Si capacitors is examined. The results allow for claiming that attained quality of the CaF_2 films is adequate for application as a barrier layer in microelectronics.

1. Introduction

Development of non-linear components compatible with Silicon technology and enhancement of integration level of industrial MISFETs are very important problems of modern microelectronics.

Along with various high-ε oxides like HfO_2, crystalline calcium fluoride (CaF_2) can be considered a promising candidate for application as a gate dielectric in MISFETs. This material has a fair dielectric constant ($\varepsilon = 8.43$), plus large values of the carrier effective mass ($1.0m_e$) and band offsets at the CaF_2/Si interface (Fig. 1, left) [1], making the gate leakage low [2]. Also, a good matching between the lattice parameters of Si and CaF_2 opens wide perspectives of 3D integration and planar miniaturization. Beyond MISFET, a possibility of employing CaF_2 as a barrier layer in super-lattices and resonant-tunneling diodes (in combination with CdF_2 or Si) has been discussed in the literature [3]. Overall quality of the fluorite films fabricated previously has been sufficient for demonstration of device operation in general. But it was not clear to what extent a transport through thin CaF_2 layer corresponds to an ideal MIS structure model.

In this work we perform a detailed characterization of the injection properties of tunnel-thin CaF_2 layers and manifest the level of CaF_2 fabrication technology achieved by now. Although consideration of MIS capacitors may seem less impressive than of complex devices, namely these structures are the most suitable for straightforward analysis of the insulator layer properties.

2. Samples. Initial Diagnostics of CaF_2 Layers

Our study is performed on Au/CaF_2[3-7 ML]/Si(111) metal-insulator-semiconductor (MIS) diodes (1 monolayer (ML) = 0.315 nm). High-quality calcium fluoride layers have been grown by molecular-beam epitaxy (MBE) at 250 ^oC, as described in [2]. By choosing a rather low temperature, formation of triangle pinholes has been avoided. Also, the growth conditions have been optimized by using Si wafers with minimal (< 20') miscut. As confirmed by atomic-force microscope (AFM) measurements, this allowed for obtaining ultra-thin CaF_2 layers with very small thickness fluctuations σ_d, sometimes even less than 0.1 nm. Correlation length for these fluctuations is about 50 nm.

The breakdown field F_{br} of CaF_2 layers is about 10^7 V/cm, which is comparable to that of SiO_2.

3. Arrangement of Experiment and Simulation

The experimental part of this work includes electrical and optical characterization of MIS capacitors with CaF_2. Their CV- and static IV-characteristics have been measured in a dark and under red laser irradiation. Further, a hot-carrier-related luminescence in the Au/CaF_2/p-Si(111) structures at different gate voltages and photon energies has been analyzed. The details around the installation and equipment were given in [4].

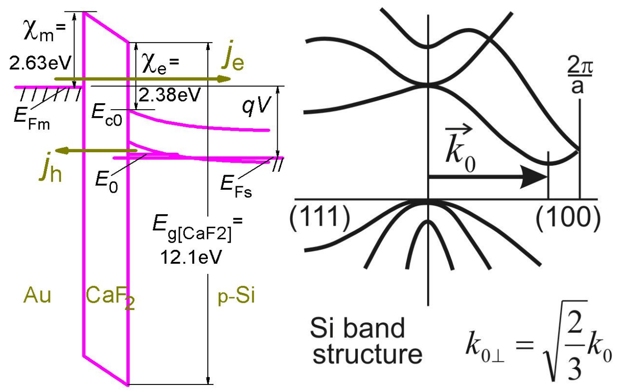

Fig.1. Left: simulated band diagram of MIS structure with CaF_2. Right: fragment of Si band structure.

The key issue of our simulation technique is accounting for the shift k_0 of the Si conduction band minima, which is essential in the case of (111) orientation (large in-plane component $k_{0\perp}$, Fig. 1). When calculating the tunneling probability $T(E, E_\perp)$, conservation of a large transverse momentum of each involved electron is regarded. Then the probability undergoes averaging over all states in the k-space with the given full and transverse energy. Also, the real barrier parameters of the Si/CaF_2 system [1] are used in the simulations, with no fitting factors. The simulations have been performed both with the laboratory program and the adapted professional software yielding similar results.

4. Discussion on Electrical Characteristics

The fabricated structures with CaF_2 were proven to exhibit all the features expected for a tunnel MIS capacitor [5]. In particular, inversion, depletion and accumulation regimes are discernable both in CV- (not shown) and IV- (Figs. 2-3) characteristics. In accumulation mode, a current rise is observed, while in the inversion-depletion polarity a plateau is present due to minority-carrier deficiency. Outside the plateau region the current is strongly dependent on the insulator thickness, which is natural for a tunnel MIS structure. A reasonable theory-to-experiment agreement allows concluding that the tunnel carrier transport dominates in the examined samples.

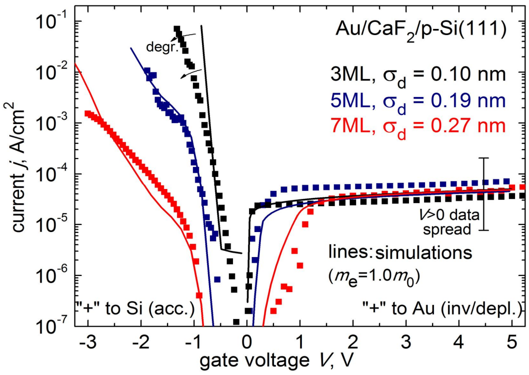

Fig.2. IV-characteristics of $Au/CaF_2/p$-Si(111) structures.

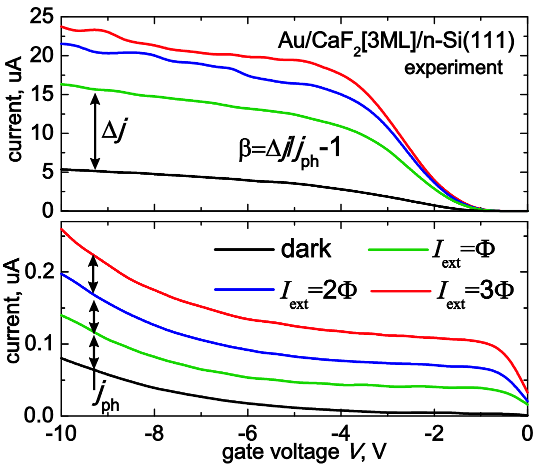

Fig.3. IV-characteristics of fresh (top) and completely degraded (bottom) reversely-biased $Au/CaF_2/n$-Si(111) structure in a dark and under external irradiation.

In Fig. 3 we demonstrate that the reversely-biased $Au/CaF_2/n$-Si(111) structure can amplify the photocurrent appearing under external irradiation, therefore operating as a phototransistor with tunnel MIS emitter. Owing to an asymmetry between the barriers for conduction band and valence band transport, external generation of even small amount of holes leads to a strong increase in dominating electron current component j_e and, consequently, the total current through the CaF_2 layer. During electrical overload a photo-response magnitude diminishes down to the photocurrent value. Comparison of the photo-responses for the fresh and completely degraded structures allowed us to estimate the current gain β: it can reach 10^3.

5. Discussion on Optical Characteristics

The substrate bias dependences of the intensities of electroluminescence signal measured at a fixed wavelength (re-calculated into the photon energy) on forward-biased $Au/CaF_2/p$-Si(111) structure are given in Fig. 4. This effect known from SiO_2 diodes [6] has now been firstly observed for CaF_2-based structures. The light emission is due to hot electrons injected through the tunnel-thin CaF_2 layer. They predominately loss their energy for phonon scattering but can be involved into recombination (RR), intra-band (IB) and intra-band direct (IB-d) radiative transitions.

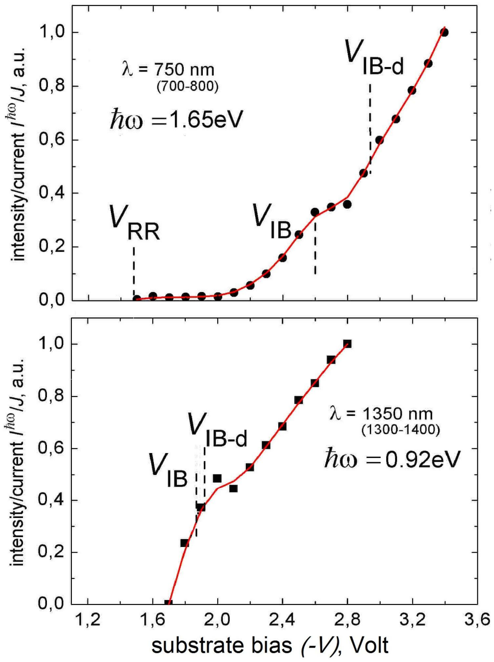

Fig.4. Luminescence intensity from $Au/CaF_2/p$-Si(111) diodes for the photon energy above (top) and below $E_{g[Si]}$ (bottom). Markers indicate the estimated thresholds for different mechanisms.

An agreement of the activation thresholds of these transitions to their estimated values further approves good injection properties of our CaF_2 films. Along with the electrical characterization (Section 4) this result evidences for prevalence of tunnel mechanism in carrier transport.

6. Conclusions

A behavior of MIS capacitors with epitaxially grown ultra-thin CaF_2 films was shown to agree with theoretical prediction in different aspects. It is essential for application of this material as a barrier layer in industrial devices.

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