Semiconductors, 2023, Vol. 57, No. 2

Changing the Parameters of MIS Structures with REE Compounds under Conditions of High Humidity

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Received September 14, 2022
Revised February 1, 2023
Accepted February 2, 2023

The properties of MIS structures with yttrium, neodymium, samarium fluorides on germanium, neodymium and samarium fluorides on *n* and *p* silicon substrates, as well as Al-Y_2O_3-*n*Si, Al-Y_2O_3-*p*Si structures under conditions of high ambient humidity were studied. Additionally, the structures were exposed to an electric field of $\sim 0.5-4$ MV/cm. For MIS structures with films of yttrium, neodymium, and samarium fluoride on germanium, as well as neodymium and samarium fluoride on *n* and *p* silicon substrates, a clear increase in the maximum specific capacitance with increasing relative humidity of the medium is observed. It has been found that the incorporation of water into the structure of the REE film fluorides studied in this work is sorption and does not cause irreversible changes in the dielectric film at the studied temperatures.

Keywords: MIS structure, silicon, germanium, density of surface states, humidity.

DOI: 10.21883/SC.2023.02.55951.4124

1. Introduction

The reliability of devices based on metal–insulator–semiconductor (MIS) structures depends strongly on the properties of the gate dielectric. In recent years, well-studied insulators (SiO_2 and Si_3N_4) are being replaced by layers with a high dielectric constant (k), since more compact field-effect MIS transistors are needed. Oxides and fluorides of rare-earth elements (REEs) belong to the group of so-called high-k dielectrics, which have been studied extensively in the last few years. They are thermally stable and typically feature high dielectric constant values and a considerable conduction band offset with silicon and germanium. These materials are compelling candidates for application as gate dielectrics in field-effect transistors and other devices based on MIS structures [1,2].

It is of interest in this context to examine the properties of REE oxides and fluorides intended for devices based on MIS structures with the purpose of identifying the optimum dielectric among REE compounds. A separate issue is the analysis of these materials in terms of influence of ambient humidity on their properties.

Moisture ingress is a well-known factor that may cause failure of integrated circuits (ICs). An epoxy mold compound is often used to protect ICs from such environmental factors as moisture and gases. However, this protective encapsulation of semiconductor microcircuits does not solve the problem of moisture ingress along interfaces or diffusion through packaging materials. Even a small amount of water may alter significantly the characteristics of dielectric materials [3]. Since moisture is inevitably present in the current standard process of fabrication of complementary MOS (metal–oxide–semiconductor) IC elements, stability against moisture sorption is an important characteristic of a gate dielectric with a high k [4]. In addition, moisture turns into high-pressure vapor in the process of soldering, thus possibly altering the design parameters of electronic devices [5]. High humidity levels may cause direct damage to electronics directly (e.g., induce delamination of printed circuit boards).

At the same time, the sensitivity of MIS structures to moisture may potentially be utilized to design humidity detectors. The influence of air humidity on the capacity of Mo$-SiO_2-NN^+$Si(111) MIS structures with a thin porous oxide with a thickness of ~ 5 nm was observed experimentally in [6]. The variation of surface conductivity of silicon dioxide induced by changes in the ambient humidity was proposed to be used as a basis for construction of a high-sensitivity sensor with a field-effect MOS transistor [7]. The sensitivity of an Au/CeO_2/Si(111) structure to the ambient humidity is attributable to an increase in the dielectric constant of a thick CeO_2 layer and to the presence of oxygen vacancies in this layer [8]. A thin-film potentiometric sensor based on a Pt/LaF_3/Sn/SiO_2/Si structure was presented in [9], where its electromotive force was demonstrated to vary depending on relative humidity. Thus, various designs of humidity sensors based on MIS structures have already been proposed.

Therefore, the study of variation of electric parameters of MIS structures based on dielectrics with a high dielectric constant under exposure to electrical overload and a humid environment and the assessment of reliability of methods for examination of a semiconductor–dielectric interface are currently relevant tasks [10].

The aim of the present study is to analyze the physical features of MIS structures with yttrium, neodymium, and samarium fluorides on germanium; neodymium and samarium fluorides on *n* and *p* silicon substrates; and

Al-Y_2O_3-*n*Si and Al-Y_2O_3-*p*Si structures and examine their properties under high ambient humidity.

2. Experimental samples

Single-crystal *n* or *p*-type mboxKEF-5 and KDB-4.5 silicon wafers with orientations (111) or (100), respectively, served as substrates. Germanium MIS structures were fabricated on single-crystal *n*type GES-2 (111) germanium wafers.

Dielectric REE fluoride films were prepared by thermal spray deposition of powdered REE fluorides in vacuum under a pressure of $\sim 10^{-5}$ Torr at a substrate temperature of $\sim 300°$C. REE fluoride films have fairly stable and reproducible characteristics and a polycrystalline structure.

Thermal evaporation of metallic yttrium was performed using a vacuum deposition setup under a pressure on the order of 10^{-5} Torr. Metal films were oxidized in a flow of dry oxygen or in air in a laboratory-type furnace at a temperature of 500−800°C within 20−30 min. Polycrystalline films of yttrium oxide with a uniform thickness and a near-stoichiometric composition were obtained this way.

The thickness of dielectric materials was 250−350 nm in each case. Aluminum electrodes 0.5−0.7 mm in diameter were deposited onto a dielectric by thermal evaporation in vacuum through a mask to fabricate MIS capacitances.

3. Experimental results

In order to examine the variation of electrophysical parameters induced by moisture absorption, a measurement probe with the studied MIS capacitance sample was introduced into a special chamber and exposed to high-moisture atmospheric environment at a temperature of 25−45°C. The parameters of MIS structures were calculated by analyzing their $C-V$ characteristics measured at a frequency of 1 MHz.

The analyzed structures were additionally exposed to electrical overload (electroforming) in high-intensity (0.5−4 MV/cm) electric fields. This simultaneous exposure to a humid environment and high-intensity electric fields speeds up the processes of degradation in electronic structures and reveals their key features.

The process of electroforming consists in the formation of a conduction channel in a dielectric under the influence of high-intensity electric fields V_{cr}. However, this state is reversible, and the studied MIS structure could be switched back to the dielectric state by reversing the polarity of applied voltage. Multiple switching of structures from the dielectric state to the conducting one and back was examined in this case, since MIS structures with REE fluoride and oxide films have the capacity for bistable switching [11,12]. The structure returns to the dielectric state after each electroforming cycle, but its density of surface states and effective charge change every time. A greater set of experimental data is formed this way.

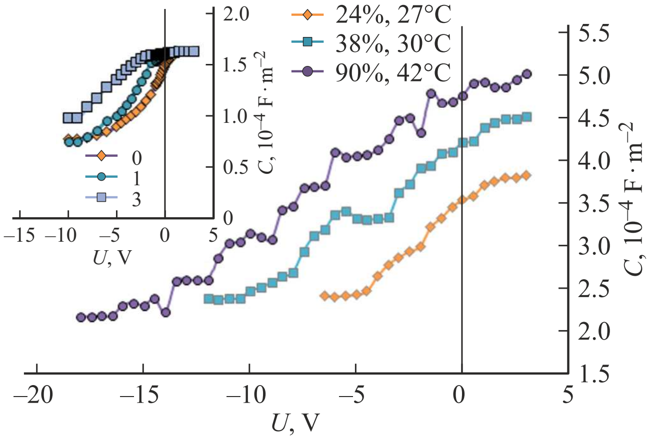

Figure 1. Voltage dependences of the specific capacitance of an Al-YF_3-*n*Ge MIS structure at different values of relative humidity and ambient temperature. The $C-V$ characteristic of a MIS structure with the same dielectric measured at a constant ambient humidity (35%) and room temperature (the number of electroforming cycles is indicated below the curves) is shown in the inset.

Figure 1 presents the voltage dependence of the specific capacitance of an Al-YF_3-*n*Ge MIS structure at different values of relative humidity and ambient temperature. The $C-V$ characteristic of a MIS structure with the same dielectric measured at a constant ambient humidity (35%) and room temperature is shown in the inset. In both cases, structures were subjected to electroforming (the number of electroforming cycles is indicated below the curves in the inset). The number of electroforming cycles increases alongside with the relative ambient humidity in the plots in the main panel of Fig. 1.

At a constant ambient humidity (35%) and room temperature, $C-V$ characteristics shift to the left along the voltage axis as the number of electroforming cycles increases. This is indicative of an increasing positive charge of the structure. The maximum specific capacitance remains the same in all electroforming cycles. When the relative humidity and ambient temperature were varied (see Fig. 1), the maximum specific capacitance was found to increase markedly with ambient humidity. This is attributable to the growth of the dielectric constant of the structure and is indicative of moisture adsorption (penetration of moisture into the bulk of the dielectric material; i.e., diffusion of water molecules). Since the dielectric constant of a film of $YF_3 \sim 14$ and the dielectric constant of water ~ 81, the overall dielectric constant of the composite material increases. It was noted that the maximum capacitance and the dielectric constant of structures return to their initial values after drying in air. Characteristics of all the studied structures with REE fluoride films were comparable to those shown in Fig. 1.

Similar phenomena were observed in [13] in the study of electrophysical properties of an Al/*por*-Si/*n*Si/ structure. The effective dielectric constant of a *por*-Si layer and the

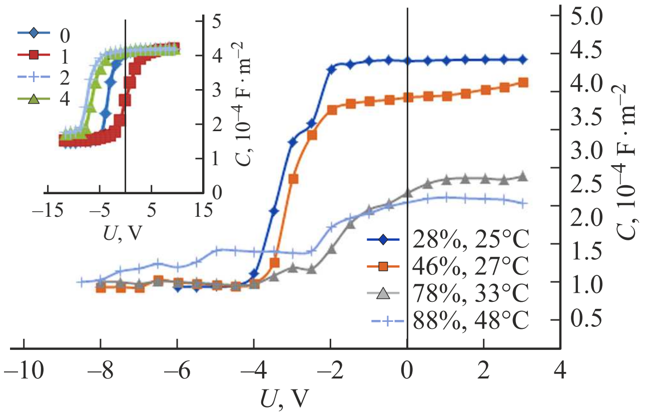

Figure 2. Voltage dependences of the specific capacitance of an Al-Y_2O_3-*n*Si MIS structure at different values of relative humidity and ambient temperature. The $C-V$ characteristic of a MIS structure with the same dielectric measured at a constant ambient humidity (35%) and room temperature (the number of electroforming cycles is indicated below the curves) is shown in the inset.

capacitance of the structure increased with relative humidity. The sensitivity of metal–nanoscale silicon oxide–silicon structures to moisture was examined in [14]. It was noted that the growth of the measured capacitance of structures at higher air humidity levels is generally attributable to the adsorption of water molecules by a thin porous oxide layer. This leads to an increase, on the one hand, in the dielectric constant of this layer (upon condensation in micropores) and, on the other hand, in the density of surface states of the silicon–oxide interface.

It is common knowledge that the effect of moisture on a dielectric also varies depending on the way in which water enters its structure. Two forms of binding of water with solids (sorption and chemical) are known. Water penetrating into the bulk of a material in the process of sorption does not become incorporated into its structure and does not cause irreversible effects; its presence or removal does not lead to the formation of a new material structure. The chemical (crystalhydrate) form of binding of water with a dielectric gives rise to new substances with different physical properties and initiates structural changes and rearrangement of the crystal lattice.

Thus, it is evident that water enters the structure of examined film REE fluorides via sorption and does not induce irreversible changes in REE fluoride films at the probed temperatures. It was found that the same is true for MIS structures with yttrium, neodymium, and samarium fluorides on germanium and neodymium and samarium fluorides on *n* and *p* silicon substrates.

Figure 2 presents the capacitance–voltage curves of an Al-Y_2O_3-*n*Si MIS structure at different values of relative humidity and ambient temperature. The $C-V$ characteristic of a MIS structure with the same dielectric measured at a constant ambient humidity (35%) and room temperature is shown in the inset. Just as in Fig. 1, $C-V$ characteristics measured at a constant ambient humidity (35%) and room temperature shift to the left as the number of electroforming cycles increases. This is indicative of an increasing positive charge of the structure. The maximum specific capacitance remains unchanged in the inset, but varies with humidity in the main panel of Fig. 2. However, in contrast to the data from Fig. 1, the maximum specific capacitance and the overall dielectric constant of the Al-Y_2O_3-*n*Si structure decrease with increasing relative humidity. This is associated with the probable formation of an additional SiO_2 layer with a low dielectric constant, which reduces the overall dielectric constant of the structure, at the silicon/yttrium oxide interface. Moisture may induce structural changes, which are governed by more complex processes than those occurring in the case of REE fluorides, at the dielectric–silicon interface in this context. Notably, an Al-Y_2O_3-*p*Si structure was similar to all the other studied structures in that its maximum specific capacitance and overall dielectric constant increased with relative humidity. This issue warrants further study; it is not unlikely that the difference is attributable to technological specifics of fabrication of particular silicon MIS structures.

It was found in the examination of a La_2O_3 film annealed in N_2 in [10] that moisture adsorption results in a reduction in the dielectric constant after several hours of exposure to air, since the dielectric constant of forming $La(OH)_3$ is lower. It was concluded that moisture adsorption is the probable cause of spread of k values of La_2O_3 films. In addition, it was determined that moisture adsorption leads to an increase in the surface roughness of La_2O_3 films on silicon.

Experimental specific capacitance values for MIS structures with REE oxides and fluorides were used to calculate the voltage dependence of the surface potential. The magnitude of variation ΔV_{fb} of the flat-band voltage was then determined as the difference between voltages corresponding to zero values of surface potential φ_s.

The surface density of the trapped effective charge with concentration N_f in an REE oxide (fluoride) film was determined as

$$Q_f = eN_f = \Delta V_{fb} C_d, \tag{1}$$

where C_d is the specific capacitance of a dielectric and e is the elementary charge.

If the dependence of the surface potential on voltage U is known, one may calculate the distribution of surface-state density D_{it} in the band gap of a semiconductor using the following formula:

$$D_{it} = \frac{C_d}{e^2}\left(\frac{dU}{d\varphi_s} - 1\right) + \frac{C_s}{e^2}, \tag{2}$$

where C_s is the specific capacitance of the space-charge region of silicon or germanium.

Figure 3 presents the dependences of the surface density of effective charge on the relative ambient humidity (RH)

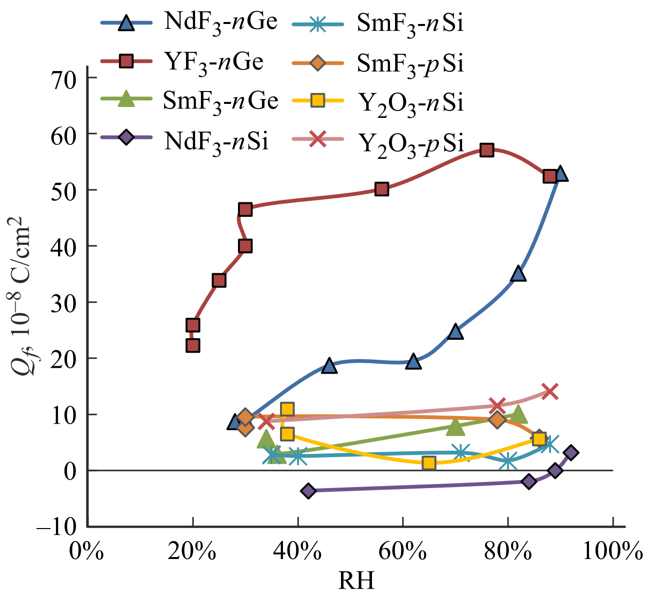

Figure 3. Dependences of the surface density of effective charge of the studied MIS structures on the relative ambient humidity.

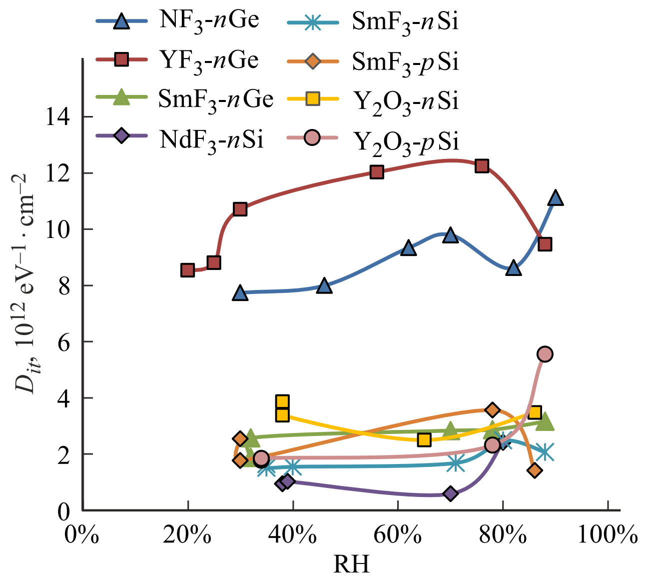

Figure 4. Dependences of the surface-state density on the surface of germanium (silicon) in the studied MIS structures on the relative ambient humidity.

for various studied structures. The positive charge density grows with increasing relative ambient humidity (and with simultaneously increasing number of electroforming cycles) in all cases. The maximum surface density of effective charge is achieved at higher RH levels in structures with YF_3 and NdF_3 films on germanium substrates. The enhancement of the positive charge density in germanium MIS structures with an SmF_3 film is much less pronounced. The range of variation of the effective charge density in MIS structures on silicon substrates is narrower, suggesting that the substrate exerts a considerable influence on this process. Therefore, it is of interest to analyze the issue of formation of surface states on a semiconductor surface in the context of moisture absorption by the studied MIS structures.

Figure 4 shows the dependences of the surface-state density of different studied MIS structures with REE oxides and fluorides on the relative ambient humidity. The data presented in Figs. 3 and 4 are obviously correlated.

Figure 5 shows the variation of the surface-state density with surface density of effective charge of the studied MIS structures at different ambient humidity levels (as was already noted, these structures were also exposed to high-intensity electric fields). It can be seen that the surface-state density at the dielectric/semiconductor interface increases with effective positive charge density.

One needs to compare this plot to a similar one for MIS structures kept at a constant ambient humidity of 35% and room temperature (see Fig. 6) to determine whether the ambient humidity affects the formation of these

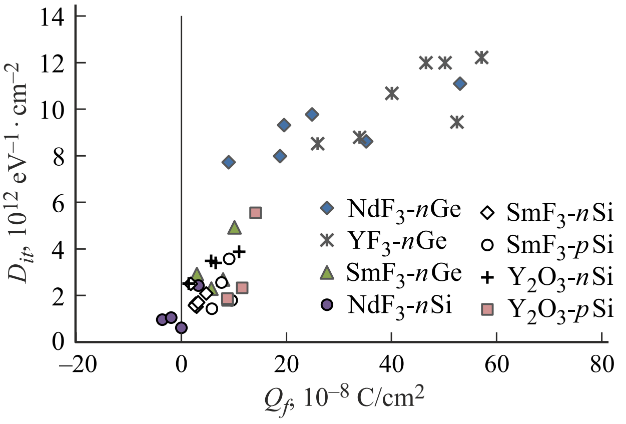

Figure 5. Dependence of the surface-state density at the REE fluoride (oxide)–germanium (silicon) interface on the surface density of effective charge at different ambient humidity levels.

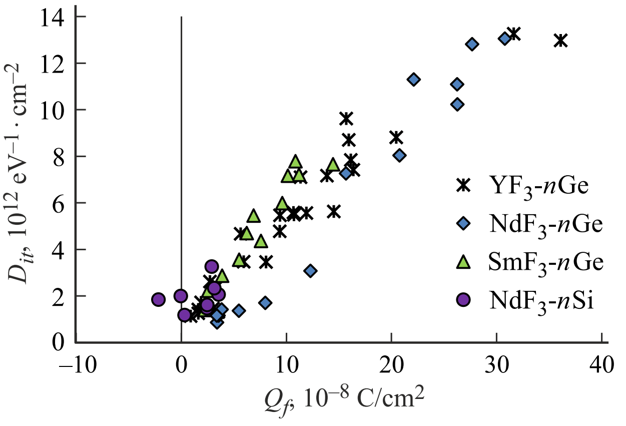

Figure 6. Dependence of the surface-state density at the REE fluoride (oxide)–germanium (silicon) interface on the surface density of effective charge at an ambient humidity of 35% and room temperature.

surface states. The plot in Fig. 6 represents the data for germanium MIS structures with YF_3, NdF_3, and SmF_3 films and a silicon structure with an NdF_3 film. Different points correspond to a series of electroforming cycles.

It is evident that the plots in Figs. 5 and 6 match in general. Specifically, just as in the presence of moisture, the surface-state density achieved in germanium MIS structures with yttrium and neodymium fluoride films is higher than the one in structures with samarium fluoride. The maximum surface-state density is the same in both cases: $\sim 1.3 \cdot 10^{13}\,\mathrm{eV}^{-1} \cdot \mathrm{cm}^{-2}$. The maximum surface-state density for a germanium structure with a samarium fluoride film is lower in both plots. The surface-state density for an Al-NdF_3-nSi structure is near-minimum in both plots, and both positive and negative effective charges are observed in this case. As was demonstrated in [11,12], the electrical parameters of MIS structures on germanium and silicon substrates deteriorate under electrical overload, while the surface-state density at the semiconductor/REE fluoride (oxide) increases.

Figures 5 and 6 present a set of data obtained within a wide range of effective charge densities and surface-state densities for the studied MIS structures. A near-linear dependence of the surface-state density at the REE fluoride (oxide)–germanium (silicon) interface on the surface density of effective charge is seen. It is known that $C-V$ characteristics „stretch" along the voltage axis as the surface-state density increases, thus altering both the flat-band voltage and $dU/d\varphi_s$. All this affects the values of D_{it} (see formula (2)).

A more thorough comparison of Figs. 5 and 6 reveals several differences. The range of variation of the surface density of effective charge in the presence of moisture is wider. Specifically, the density of effective charge at the maximum surface-state density of $\sim 1.3 \cdot 10^{13}\,\mathrm{eV}^{-1} \cdot \mathrm{cm}^{-2}$ reaches a value of $57 \cdot 10^{-8}\,\mathrm{C} \cdot \mathrm{cm}^{-2}$ in a humid environment, while the maximum density of effective charge at a constant ambient humidity is $36 \cdot 10^{-8}\,\mathrm{C} \cdot \mathrm{cm}^{-2}$. Thus, high-frequency $C-V$ measurements reveal that the surface density of effective charge increases in the presence of moisture.

An increase in the surface density of effective charge in measurements with a varying ambient humidity (relative to similar measurements performed at a constant ambient humidity) may be indicative of formation of both new surface states and charge centers in the bulk of a dielectric and in the region adjacent to a semiconductor. It is not possible to separate experimentally the contributions of electrical overload and a humid environment to the growth of the measured surface-state density. An increase in the surface-state density coinciding with an increase in the ambient humidity has already been noted in scientific literature. For example, the influence of humidity on a Mo$-SiO_2-nn^+$Si(111) structure with an oxide layer with a thickness of ~ 5 nm was examined in [11]. The observed growth of the surface-state density with increasing relative humidity was linear in this case.

Thus, the surface-state density change occurring in the process of electroforming in a high-intensity field probably gets enhanced in the presence of moisture, thus inducing the formation of additional surface states at the REE fluoride (oxide)/semiconductor interface and contributing to an increase in the surface density of effective charge.

4. Conclusion

MIS structures with yttrium, neodymium, and samarium fluorides on germanium; neodymium and samarium fluorides on n and p silicon substrates; and Al-Y_2O_3-nSi and Al-Y_2O_3-pSi structures were studied; their properties under high ambient humidity were examined. The analyzed structures were additionally exposed to electrical overload (electroforming) in high-intensity (0.5–4 MV/cm) electric fields. This simultaneous exposure to a humid environment and high-intensity electric fields speeds up the processes of degradation in electronic structures and reveals their key features.

The maximum specific capacitance of MIS structures with yttrium, neodymium, and samarium fluorides on germanium and neodymium and samarium fluorides on n and p silicon substrates increased markedly at higher relative ambient humidity levels. This is associated with an increase in the dielectric constant of the structure and is indicative of moisture absorption. It was found that water enters the structure of examined film REE fluorides via sorption and does not induce irreversible changes in dielectric films at the probed temperatures.

The maximum specific capacitance and the overall dielectric constant of the Al-Y_2O_3-nSi structure were found to decrease with increasing relative humidity. This may be attributed to the formation of an additional SiO_2 layer, which has a lower dielectric constant and reduces the overall dielectric constant of the structure, at the silicon/yttrium oxide interface. Moisture may induce structural changes, which are governed by more complex processes than those occurring in the case of REE fluorides, at the dielectric–silicon interface in this context.

It follows from the results of analysis of high-frequency $C-V$ measurement data that the surface density of effective charge increases in the presence of moisture. The surface-state density change occurring in the process of electroforming in a high-intensity field probably gets enhanced in the presence of moisture, thus inducing the formation of additional surface states at the REE fluoride (oxide)/semiconductor interface and contributing to an increase in the surface density of effective charge.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin