Kelvin-probe microscopy as a technique of estimation of the charge traps saturation time

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Abstract. In this work, a method for estimating the saturation time of traps in dielectric layers based on the KPM is proposed. Using hafnium oxide layers as an example, it is shown that when charging with a series of points with different durations, a different dependence of the residual potential on time is observed. It is assumed that this technique makes it possible to evaluate the performance of devices based on dielectric layers.

1. Introduction
At present, the search and investigation of materials with a high dielectric constant – high-k dielectrics – continues. Hafnium oxide is promising as a gate dielectric in field-effect transistors, MOS structures [1], an active medium in flash memory devices [2-4], as well as in non-volatile resistive memory elements (Resistive Random Access Memory, ReRAM) [3]. The mechanism of charge transport in high-k dielectrics is the subject of active research [2-5]. It was shown that charge transport in dielectrics occurs through defects (traps) capable of changing the charge state. Resistive memory is fast (~ 0.1–10 ns) (for comparison, the reprogramming time of a conventional flash memory is 1 ms), consumes little power (6 fJ/bit during switching), has a high number of reprogramming cycles (at least $10^{12}$) compared to $10^4$ cycles for conventional flash memory, stores information for 10 years at 85 °C, is radiation resistant.

It is also possible to use HfO$_2$ layers in ferroelectric random access memory (FeRAM) elements [6, 7]. HfO$_2$ films demonstrate stable ferroelectric properties at thicknesses up to 10 nm [13], and they are also compatible with CMOS technology.

The purpose of this work is to develop a technique for assessing the rate of charge localization in thin HfO$_2$ films on silicon.

2. Samples and methods
The measurement of the dependence of the accumulated charge on the potential application time was carried out on an atomic force microscope (AFM) NTegra Aura (NT-MDT, Moscow, Russia) with Kelvin probe microscopy (KPM) technique using commercial conductive probes HA_FM/W$_2$C (NT-MDT). The measurements were carried out as follows. Regions with a uniform potential distribution were selected on each of the images. In this area, charges were injected in a series of points. For injection, a potential of ± 7 V was used on the probe, which is guaranteed to exceed the possible barriers in the "probe – sample – ground electrode" circuit. The injection was carried out by bringing the probe with the potential applied to it into direct contact with the surface. The charging (contact) time varied from several tens of milliseconds to several tens of seconds. Obviously, with a decrease in...
the charging time, the amount of injected charge decreases, therefore, charging was performed with
the longest time first. After that, the probe was retracted from the surface, shifted to the side by ~ 1 μm, and the procedure was repeated with the next, shorter time. For accurate control of the injection time, an AFM built-in oscilloscope was used, which recorded the time when the amplitude of the forced oscillations of the probe vanished in direct contact with the surface. After the injection, the region was scanned again, and the image of all charge spots was recorded. The scanning speed was selected in such a way that the registration of charge spots occurred approximately 1 minute after charging the last point. To test the proposed technique, we selected samples of polycrystalline HfO2 films.

In this work, we studied samples that were HfO2 films with a thickness of about 40 nm on the n-Si (100) surface. The films were synthesized using TEMAH precursors (tetrakis(ethylmethylamide) hafnium (IV), Hf(NCH3C2H5)4) in combination with H2O at a substrate temperature of 250 °C [8]. After synthesis, one of the samples was annealed in situ in an N2 flow for 1 hour at a temperature of 700 °C. After annealing, the sample was slowly cooled in the reactor to room temperature. The synthesized HfO2 films are polycrystalline with crystallites of the monoclinic phase.

The cathodoluminescent (CL) properties of the films and the dynamics of the absorbed electron beam current were studied on a CAMEBAX electron probe microanalyzer (Cameca, France) equipped with an original optical spectrometer for recording cathodoluminescence spectra [9]. The electron beam energy of 2.5 keV was used, which corresponds to the penetration depth of about 30 nm. The electron beam current was 8 nA, while the electron beam diameter was 5 mm. The method for measuring the absorbed current is described in detail elsewhere [10].

3. Results and discussion
Before carrying out the KPM studies, the samples were examined by the CL method. Figure 1(a) shows the CL spectra of the initial (black curve) and annealed (blue curve) samples.

![Figure 1](image_url)

**Figure 1.** (a) CL spectra of the initial (black curve) and annealed samples (blue curve). (b) Dynamics of the absorbed current upon switching on the electron beam on the initial (black curve) and annealed (blue curve) samples.
It can be seen that annealing in a nitrogen atmosphere leads to a twofold increase in the CL intensity. In the literature [8, 11] it is considered that the luminescence of HfO$_2$ in the visible range is associated with oxygen vacancies. It is also assumed in [8] that it is oxygen vacancies that are traps for charge carriers.

This is confirmed by the conducted studies of the dynamics of the absorbed current (see figure 1b). It can be seen that the behavior of the absorbed current in the initial sample (black curve) differs significantly from that in the annealed sample (blue curve). In the initial sample, a fairly fast localization of negative charges and a much slower process associated with the localization of positive charges are observed. The method described in [10, 12] was used to estimate the localization time of the charge and the localized charge. The data obtained in various experiments were averaged; the average values are given in Table 1.

**Table 1. Localization time $t$ and localized charge $Q$ for initial and annealed samples.**

| Sample    | Positive charge | Negative charge |
|-----------|-----------------|-----------------|
|           | $t$             | $Q$             | $t$             | $Q$             |
| Initial   | 15±2 s          | 38±10 nC        | 6±1 s           | 9±2 nC          |
| Annealed  | 16±2 s          | 110±10 nC       | 8.5±2 s         | 12±3 nC         |

After annealing, the contribution of electron traps decreases noticeably. The above arguments indicate that these samples should exhibit differences in the temporal characteristics of the charge accumulation processes.

![Figure 2](image-url) **Figure 2.** Side-view of the potential distribution pattern after charging with a potential of +7V of a series of points of the initial (a) and annealed (b) samples. The figure shows the charging time for each of the points.

Let us first simply describe results obtained after charging several points with positive and negative potential on both samples.

Results of charging the surface with a probe with a potential of +7V are shown in figure 2 for the initial (figure 2a) and annealed samples (figure 2b). The images are a side-views of the potential pattern, so that the dependence of the residual potential in the spots on the charging time is obvious. It is easy to see that in the annealed sample, the residual charge after charging for 13 sec is higher almost 2 times. On the other hand, in the initial sample, the dependence of the residual potential on the charging time is much less pronounced. Note that an increase in the charge injection time leads also to an increase in the area of the charge spot and, as a consequence, suppression of diffusion from the center of the spot.
Figure 3. Side-view of the potential distribution pattern after charging with a potential of -7V of a series of points of the initial (a) and annealed (b) samples.

In the case of charging with a potential of -7V (figure 3), the dependence of the residual potential on the charging time looks somewhat different. First of all, attention is drawn to the fact that the magnitude of the potential in a charge spot with a charging duration of ~ 12 sec practically does not differ, which corresponds to the results obtained in the analysis of the dynamics of the absorbed current. In addition, in this case, the dependence of the residual potential on the charging time is relatively weakly expressed on the annealed sample, while it is clearly visible on the initial sample.

For a more accurate analysis, the data from several experiments with identical conditions (but different injection times) were summarized in the graphs shown in figure 4.

Figure 4. Dependence of the residual potential on the injection time.

It can be seen from the graphs on the figure 4 that when both samples are charged with charges of both signs, the time dependence has two sections: a weakly increasing linear (conventionally shown by lines of the corresponding colors) and a sharply increasing section at short charging times. We believe that the linear portions of the dependence of the residual potential on the injection time are associated with an increase in the diameter of the charge spots. This leads to a decrease in the probability of diffusion from the center of the spots and, as a consequence, to an increase in the residual potential even after saturation of all traps. We believe that the time at which the transition from a sharp increase to a linear segment occurs corresponds to the time of complete saturation of traps in the region under the probe. Thus, it is this time that can be used to analyze the performance of
promising dielectric layers in the future. As one can see, for positive charges on the initial sample, the
saturation time is shorter than this technique allows. For such samples, a slightly modified approach
can be used in which the minimum charging time is 100 μs.

It should be noted that the probability of charging the traps depends, among other things, on the
excitation density, which makes it impossible to compare the times obtained by different methods.

4. Conclusions
To conclude, we propose a novel technique of estimation of the charge traps saturation time. It is
shown that when charging a number of points with the same potentials for different periods of time, it
is possible to find the time at which the character of the dependence of the residual potential on time
changes. This time is proposed to use as a charge traps saturation time. Such measurements were
carried out on hafnium oxide layers before and after annealing in a N₂ atmosphere. It was found that
annealing does not affect the traps for electrons, but significantly changes the traps for holes.

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