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Charge Storage by Contact Electrification on Thin $SrTiO_3$ Film

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A novel charge storage method used contact electrification phenomenon was demonstrated on $SrTiO_3$(STO) thin films with high dielectric constant using a modified atomic force microscope(AFM). Here, a biased conductive cantilever was used to deposit the charges by contact electrification and to detect electrostatic force change induced by contact electrified charges. As a result, the writing, reading and erasing were demonstrated with small words and small dots and two adjacent positive charge dots was discriminated with the separation as small as about 63nm. These results revealed potential capability of the present system, i.e., contact electrification on STO film with a biased AFM, for high density charge storage.

1. Introduction

Charge storage in nonvolatile semiconductor memories has been used for data storage for many years. Recently, Barret and Quate[1,2] demonstrated charge storage trapped in nitride-oxide-silicon (NOS) structure using a scanning capacitance microscope (SCaM). They achieved a possible recording density of 18Mbit/mm^2 and the trapped charge was kept over a period of seven days stably. However, its bit size is limited by a spread of depletion region and by a thickness of nitride film. Moreover, tip wear caused by contacts between tip and surface may degrade reliability of data storage and their system seems to be rather complicated.

Quite recently, using a biased atomic force microscope (AFM),[3,4] we investigated dissipation of contact-electrified charges on thin $SrTiO_3$(STO) film with a high dielectric constant,[5] which, in recent years, has been paid attention for possible applications to nonvolatile memories. As a result, we clarified that the charge dissipation on STO film was slower than that of thin silicon oxide[6-8]. Further, we succeeded to decrease a size of charged area, i.e., bit size, to 70nm FWHM.

As a natural result, in the present experiment, we investigated the feasibility of thin STO film as a medium and of contact electrification as a tool for the novel charge storage with a large recording density.

2. Experimental

The STO film, which we used as a sample, with a thickness of ~60nm was fabricated on a Pt bottom electrode on MgO(100) substrate by electron cyclotron resonance (ECR) sputtering at the substrate temperature of ~400℃.

For writing, reading and erasing the electric charges on $SrTiO_3$(STO) surface, contact electrification and electrostatic force measurement were performed with a biased AFM[3,4] by the following procedure.

For the writing, as shown in Fig.1 (a), when the conductive cantilever biased at a large contact voltage V_c was made in contact with STO surface, contact-electrified charges were deposited on STO surface during scanning or contact time. Here, the Pt bottom electrode was electrically grounded. After the contact electrification, the STO surface was quickly withdrawn from the cantilever as shown in Fig.1(b).

For the reading, contact-electrified charges were imaged under the noncontact DC mode as a spatial change of electrostatic force induced on the tip of the conductive cantilever at bias voltage V_s.[4] The force change was detected as the deflection of the conductive cantilever. Here, to prevent a crash between the tip and STO surface with averaged roughness of 10~20nm, the tip-sample distance Z should be kept larger than 30nm

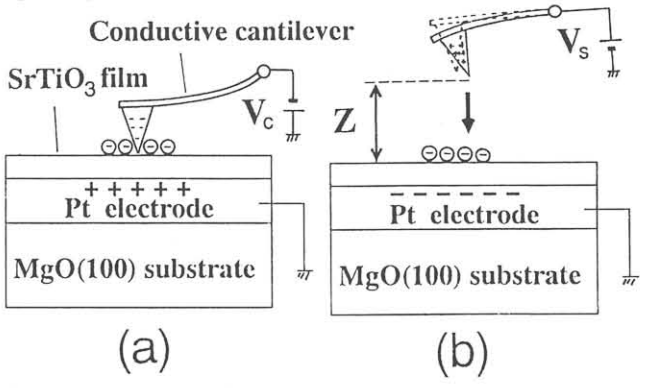

Fig.1 (a)Schematic diagram of the experimental setup for the contact electrification with the AFM.
(b)Schematic diagram of the experimental setup for the noncontact DC mode measurement of the electrostatic force with the AFM.

during the force measurement.

For the erasing, small amounts of electric charges were deposited uniformly on STO surface through the contact electrification at a small contact voltage V_c=−1V, because the deposited charges on STO surface were not erased completely by the contact with the electrically grounded conductive cantilever. Hereafter, we define this surface as the erased surface before the charge deposition.

As the conductive cantilever, we used a Si_3N_4 microcantilever with a Si_3N_4 tip coated with 500Å Au film on 15Å Cr film. It has a spring constant of 0.16N/m, a mechanical resonance frequency of 27 kHz and an averaged radius of tip curvature of R~250 Å.

3. Results and Discussion

3.1 Examples of charge storage

Figure 2 shows charge patterns of letters written on the $SrTiO_3$ (STO) surface. These letters of "STO" were written by the hand-operated scanning of the cantilever biased at V_c=−9V in contact with the STO surface. The reading was done at zero bias voltage of V_s=0V. In Fig.2, the brighter region indicates more attractive force. Thus, Fig.2 made clear that letters such as "S", "T" and "O" can be written easily within 1 micron^2 size by negative charges even with the hand-operated scanning.

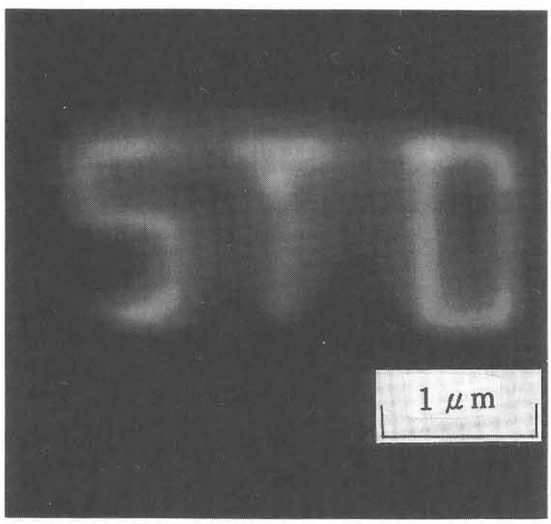

Fig.2 Charge patterns of letters of "STO" written by hand-operated scanning. V_c=−9V and V_s=0V. Here, the brighter region indicates more attractive force.

Figure 3 shows charge dots written on the STO surface in a line by alternate positive and negative charges. Here, the writing was done by scanning the cantilever straight from A to B in the time of ~3s. During scanning, the contact voltage was switched alternately at V_c=+5V and V_c=−5V in regular intervals of 200nm. The reading was done at V_s=−5V. Thus, we can write bipolar dots in a line with 200nm spacings easily.

Figure 4 shows line-scan data of charge dots written on the STO surface in a line by positive charges. The writing was done with V_c=+5V in contact time of 30 s from left to right by sequential contacts with the STO

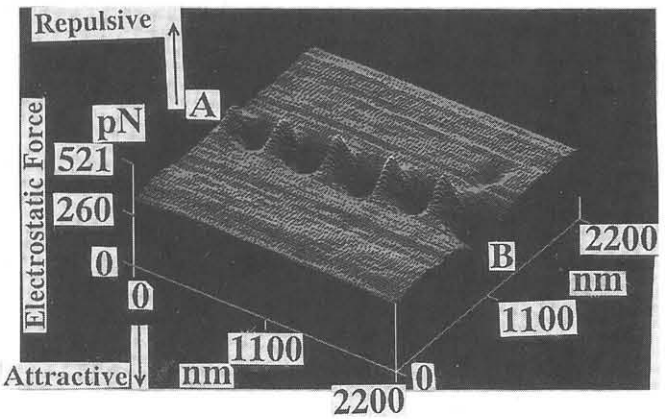

Fig.3 Charge dots written in a line by alternate positive and negative charges with V_c=+5V and V_c=−5V during the scanning time ~3s from A to B, respectively. V_s=−5V.

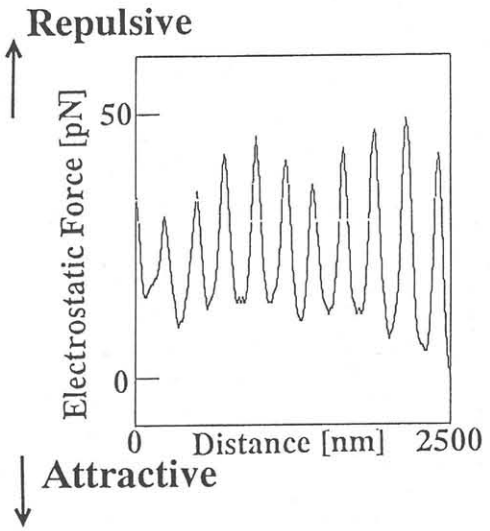

Fig.4 Scan-line data of positive charge dots in a line. V_c=+5V, contact time t_0=30s and V_s=+2V.

surface. The reading was done at V_s=+2V. The positive charges were imaged as the peaks of repulsive forces. Here, the interval of the charge dots and the FWHM of single dot are estimated to be ~230nm and ~140nm, respectively. It should be noted that each of 10 charge dots with the same polarity is clearly separated even with these small spacings. Thus one dot can be written easily by positive charge in a small area less than (250nm)^2.

3.2 Limit of writing and reading sizes by charge storage

To investigate the limit of writing and reading sizes, the spacing between two charge dots was decreased further. As a result, we found that the two positive charge dots can be still discriminated with a small spacing of ~63nm as shown in Fig.5. Here, the writing was done with V_c=+5V in contact time of 15 s from A to B by sequential contacts with the STO surface. The reading was done at V_s=0V. The positive charges were

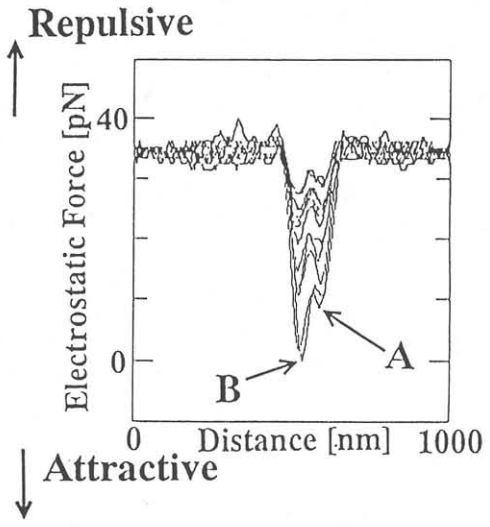

Fig.5 Adjacent positive charge dots with ~63nm spacing. V_c=+5V, t_0=15s and V_s=0V. The time interval of the time evolution is 37s.

imaged as the peaks of attractive forces.

Figure 5 also shows time evolution, at intervals of ~37 s, of line-scan data of electrostatic force change due to charge dissipations. This figure also shows the overlapping of two charge dots. Therefore, the size limit with the present setup seem to be ~60nm. There are two possible origins of this limit, i.e., the limit of real writing size and the limit of reading size. The limit of writing size may be resulted from the spread of the charges due to surface diffusion. However, the spatial change of electrostatic force in Fig.5 does not show the increase of FWHM so much as a function of time, although the peak value decreases rapidly. On the other hand, the limit of reading size may be determined from both the radius R of the tip curvature and the distance Z between the tip and the STO surface. The expected limit of reading size may be roughly given by $2\times R+Z$. Using the estimated values of R~25nm and $Z \geqq 30$nm in the present setup, the roughly estimated limit of reading size seems to be ~80nm. Therefore, we believe that the present experimental limit of ~60nm originates mainly from the limit of reading size.

Thus, to improve the reading size further, both the radius R and the distance Z should be decreased. In addition, both the cone angle of the tip and the surface roughness of the STO film should be decreased. Further, force derivative measurement by Z distance modulation may improve the reading size, because the force derivative dF/dZ will depend on the distance stronger than the force F itself.

One of the problems in the charge storage with the present setup is the holding time of the deposited charges, which is too short for the charge storage. However, the dissipation speed seems to depend on the positions of the STO surfaces, on each STO samples and on the quality of STO film. We also found that the charge dissipation is restrained in a vacuum. Therefore, to improve the holding time of the deposited charges, the dissipation mechanism of charges should be investigated further.

4. Conclusions

We investigated the possibility of thin STO film as a medium and of contact electrification as a tool for the novel charge storage with a large recording density. As a result, we revealed potential capability of the present system for high density charge storage.

Acknowledgments

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