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Preparation and Electric Properties of $PbTiO_3$ Thin Films by Low-pressure Thermal Plasma Deposition

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$PbTiO_3$ thin films were prepared by low-pressure thermal plasma deposition on (100)Pt/(100)MgO substrates. Mist of source material in which metal alkoxides are dissolved in 2-methoxyethanol was introduced into plasma through heating furnace and deposited onto substrates at 600°C. As-deposited $PbTiO_3$/Pt/MgO thin film prepared at 1.33×10^4 Pa was grown epitaxially, but was consisted of many rectangular shaped grains, with many grain boundaries and it was impossible to measure electric properties. As-deposited film prepared at 1.00×10^4 Pa showed weak peaks of X-ray diffraction and the film was not grown epitaxially. On the other hand, the film after annealed at 700°C showed strong diffraction peaks and epitaxial growth was also observed. For annealed film, moreover, no clear grain boundaries were observed. The value of ε_r, tanδ, Pr and Ec of annealed film were 160, 3.2%, 10.4 $\mu C\cdot cm^{-2}$ and 51.2 $kV\cdot cm^{-1}$, respectively. Since the composition, Pb/Ti, measured by EDS attaching to SEM changed point by point, the distribution of composition in annealed film was investigated and found out several relations between composition and electric properties. At stoichiometric composition, Pr and Ec showed the lowest value and they gradually became large as composition deviated from stoichiometric one. Moreover, the value of ε_r became gradually large as the ratio of Ti became high.

Key words : Lead Titanium oxide, Mist, Thermal plasma, Thin film

I. Introduction

Ferroelectric thin films have attracted attention for non-volatile memories and electro-optic devices. Among many ferroelectric materials, $PbTiO_3$ has a large spontaneous polarization and a relatively small dielectric constant, which allow numerous potentially important applications in the field of electronics and optoelectronics.[1] Generally the growth of epitaxial $PbTiO_3$ thin films takes place above its Curie temperature on single-crystalline substrates such as MgO.[2-4] Many preparation techniques have been used for epitaxial $PbTiO_3$ thin films on MgO(100).[2-4]

Many of the preparation techniques of thin films are deposition from gas phase and liquid phase, classified roughly into physical vapor deposition(PVD) and chemical vapor deposition(CVD). In CVD process, vapor of material is supplied onto substrates and thin films are prepared by chemical reaction at gas phase or surface of substrates, the methods that material is enhanced by plasma, laser, light and so on have been developed. Plasma used in engineering is classified into low temperature plasma and thermal plasma. It is generally known that the state of plasma changes from low temperature plasma to thermal plasma by the rise of pressure and it is thought that the boundary is about 1.33×10^3 Pa. Over 1.33×10^3 Pa gas temperature of plasma rises and the state of plasma becomes thermal plasma, especially for the pressure range approximately from 1.33×10^3 Pa to 1.33×10^4 Pa the change of gas temperature is remarkable. Near atmospheric pressure gas temperature attains maximum, plasma becomes equilibrium state and the change of gas temperature is minor. In Plasma Enhanced CVD process that uses low temperature plasma and deposits thin films at a few hundred Pa, plasma is used as source of enhancing of chemical substances. On the contrary, in the method that uses thermal plasma, plasma is not used as source of enhancing, but used as source of heat. In regard to this method, various names are found in many papers, like RF Thermal Plasma Evaporation, RF Plasma Flash Evaporation, ICP Flash Evaporation and so on.[5-8] In either case, source material is introduced into plasma, vaporized by ultrahigh temperature of plasma and the vapor is deposited onto substrates. The reason of delay of establishment and popularization in this method is that etching and abnormal grain growth in thin films are caused because temperature of plasma is too high, it is pointed out that this method is not necessarily excellent method in terms of improvement of film condition. Except for too high temperature under deposition, however, there are many advantages that it is possible to apply to thin films with complicated composition or high crystallinity and utilize low vapor pressure elements. We note the pressure range approximately from 1.33×10^3 Pa to 1.33×10^4 Pa where temperature of plasma changes remarkably by pressure. We use plasma as source of heat, but temperature of plasma is

lower than normal thermal plasma, that is caused by lower pressure than normal thermal plasma and call our preparation method as low-pressure thermal plasma deposition. In most of reports of this method, thin films are deposited over approximately 2.67×10^4 Pa, there are few reports relating to deposition for the pressure range approximately from 1.33×10^3 Pa to 1.33×10^4 Pa. Moreover, the reports relating to the preparation of $YBa_2Cu_3O_y$ superconducting thin films are mostly occupied as application of this method, there are few reports relating to ferroelectric $PbTiO_3$ thin films.

In this paper, we prepare $PbTiO_3$ thin films, evaluate properties, especially electric properties of thin films and clarify the usefulness of application of low-pressure thermal plasma deposition to the preparation of ferroelectric thin films.

II. Experimental Procedure

Schematic diagram of experimental apparatus was shown in Fig. 1. An apparatus was consisted of torch, chamber and RF generator. Torch was portion where plasma is generated and consisted of a coaxial double tube of fused silica and Cu coil wound outside of the tube. Plasma was generated by impressing alternating current to coil from RF generator operated at 8 kW and 4 MHz as input power and frequency, respectively. Cooling water was supplied between inner and outer tube in order to protect torch from ultrahigh temperature of plasma. In chamber substrate stage that substrates were placed on was fixed and heated by sheath heater. Substrate temperature was measured by thermocouple located at the back side of substrate stage. Experimental conditions were as follows. The flow rate of

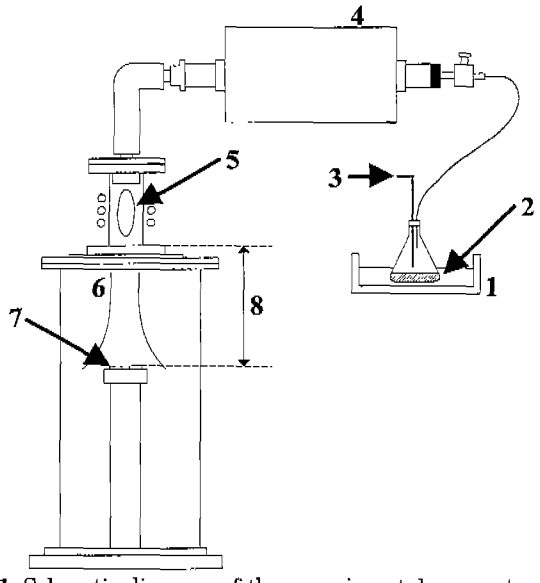

Fig. 1. Schmatic diagram of the experimental apparatus used in this study, 1: Ultrasonic nebulizer, 2: Source solution, 3: Ar carrier gas, 4: Furnace, 5: Plasma, 6: Tail flame, 7: Substrate, 8: Substrate distance.

Ar and O_2 fed into chamber were 13 and 2 $l\cdot min^{-1}$, respectively, and constant throughout all experiments and control of pressure was done by changing the rate of exhaust, the ratio of Ar to O_2 was, therefore, invariably constant. The flow rate of Ar carrier gas was 0.1 $l\cdot min^{-1}$ and was also constant. Pressure at deposition was 1.00×10^4 and 1.33×10^4 Pa, substrate temperature was 600°C and it was constant. In the case that pressure was low, plasma was the state of glow discharge and the shape of plasma changed to fusiform at approximately 1.33×10^3 Pa as the boundary by the rise of pressure. At the pressure of 1.00×10^4 and 1.33×10^4 Pa, plasma was fusiform and tail flame extends downward. The distance between plasma and substrates, hereafter this distance was defined as substrate distance, was one of important factors for deposition of thin film. We determined it was optimum that substrate distance was 12.5 cm, so it was constant throughout all experiments. Deposition time was 120 min and it was also constant. (100) Pt/(100)MgO was used as substrates. For source material using in this method, solid form like powders or liquid form like aqueous solution of nitrates and acetates can be selected.[5-8] In this work, organometallic sol in which alkoxides of each metal element were dissolved in organic solvents was used as source material. Pb solution was prepared by dissolving $Pb(CH_3COO)_2\cdot3H_2O$ in 2-methoxyethanol at 200°C and Ti solution was prepared by refluxing $Ti(i\text{-}OC_3H_7)_4$ in 2-methoxyethanol at 80°C for 12 h. Source material was prepared by controlling concentration and ratio of mixing of these two solution. The concentration of source material was normally about 0.1 $mol\cdot l^{-1}$. Identification of constituent phases of thin films were done by X-ray diffractometer using CuKα radiation(XRD; X'Pert-MPD, Philips), the crystal texture was studied by X-ray pole figure apparatus using CuKα radiation(PW-1078/50, Philips), the chemical composition of thin films was analyzed by energy dispersive spectroscopy(EDS; DX-95T, Philips) and the microstructure of thin films was observed by field emission gun:scanning electron microscope(FE-SEM; S-800, Hitachi). The electric properties of thin films were measured by impedance analyzer(4192A, Hewlett Packard) and ferroelectric test system(RT6000HVS, Radiant Technologies).

III. Results and Discussion

$PbTiO_3$/Pt/MgO thin films with stoichiometric composition were prepared under following conditions that pressure at deposition was 1.00×10^4 and 1.33×10^4 Pa and substrate temperature was 600°C. Mist of source material introduced into heating furnace and became fine particles about 1 μm by vaporization of organic solvents in mist and precipitation of solute. In the case that pressure was low, in other words, temperature of plasma was low, particles introduced into plasma were not vaporized and dropped on substrates. In the case that pressure was high(over approximately 6.67×10^3 Pa), in other words, temperature of plasma

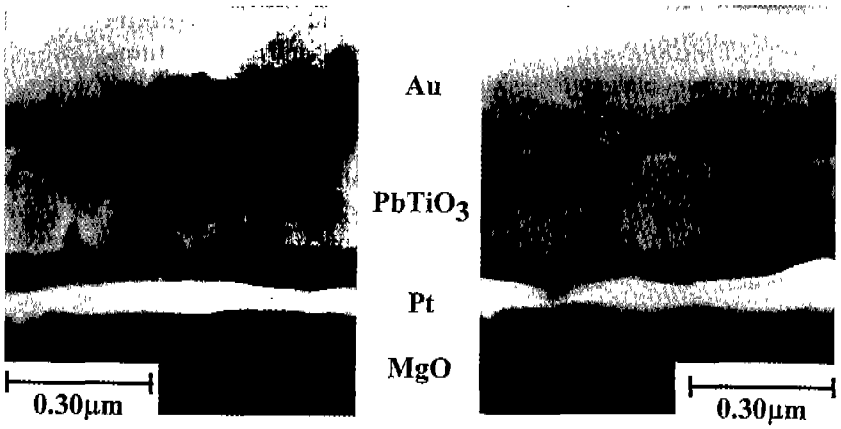

Fig. 2. FE-SEM photographs of $PbTiO_3$/Pt/MgO films pre((a) annealed at 1.00×10^4 Pa(b) as-deposited film at 1.33×10^4 Pa).

was relatively high, particles introduced into plasma were vaporized by ultrahigh temperature of plasma and the vapor was deposited onto substrates. At 1.00×10^4 Pa , (h00) and (101) peaks were detected from XRD patterns, but their intensities were low, shape of peak was blunt and the half-value width of (100) peak was wide and the degree of crystallization was low. At 1.33×10^3 Pa, only (h00) and (00l) peaks were detected from XRD patterns. Shape of peak was sharp and the full width half maximum of (100) peak was narrow and the degree of crystallization was high. From (101)X-ray pole figure of thin films, poles were indistinct at $1.00\cdot10^4$Pa, on the other hand, four poles were clearly observed at 45° on psi(ψ) axis and every 90° along phi(ϕ) axis, and it was consequently obvious that thin film was grown epitaxially at 1.33×10^4 Pa. At 1.00×10^4 Pa, moreover, it was observed that rectangular shaped grains of 0.2 μm as mean size of them were gradually growing and at 1.33×10^4 Pa, many grains shaped like island observed and unevenness of surface became remarkable by grain growth.

Thus, it was obvious that epitaxial $PbTiO_3$/Pt/MgO thin film was prepared at 1.33×10^4 Pa, but was consisted of many rectangular shaped grains and unevenness of surface became remarkable. On the other hand, $PbTiO_3$/Pt/MgO thin film with relatively smooth surface was prepared at 1.00×10^4 Pa, but its degree of crystallization was low and not grown epitaxially.

$PbTiO_3$/Pt/MgO thin films with stoichiometric composition depositing Au as upper electrode were prepared under following conditions that pressure at deposition was 1.00×10^4 and 1.33×10^4 Pa and substrate temperature was 600°C. At 1.33×10^4 Pa, the degree of crystallization of as-deposited film was high. At 1.00×10^4 Pa, however, the degree of crystallization of as-deposited film was low, so annealed at 700°C for 1 h in air, consequently the degree of crystallization of annealed film became high. FE-SEM photographs of them were shown in Fig. 2. As-deposited film at 1.33×10^4 Pa was consisted of rectangular shaped grains and grain boundaries were clearly observed shown in Fig. 2(b). Annealed film at 1.00×10^4 Pa, on the other hand, could not be found clear grain boundaries shown in Fig. 2(a). It was impossible to measure dielectric constant, loss factor and P-E hysteresis loop of as-deposited film shown in Fig. 2(b), however, it was possible to measure electric properties of annealed film shown in Fig. 2(a). Moreover, resistivity of thin films shown in Fig. 2(a) and (b) were about 10^9 and 10^2 Ω·cm, respectively. It was considered that grain boundaries became paths of current between upper and lower electrode and resistivity of as-deposited film with many grain boundaries was, consequently, much higher. The dielectric constant ε_r and loss factor tanδ at 1 MHz of annealed film shown in Fig. 2(a) were 160 and 3.2%, respectively. P-E hysteresis loop of same film was shown in Fig. 3. The remanent polarization Pr and coercive field Ec from hysteresis loop were about 10.4 μC·cm^{-2} and 51.2 kV·cm^{-1}, respectively. These values were similar to those of $PbTiO_3$ thin films prepared by MOCVD and sol-gel method and it suggested that thin film prepared by low-pressure thermal plasma deposition was good quality.[2,9] Composition of annealed film was totally stoichiometric, but distribution of composition existed in thin film by measuring point by

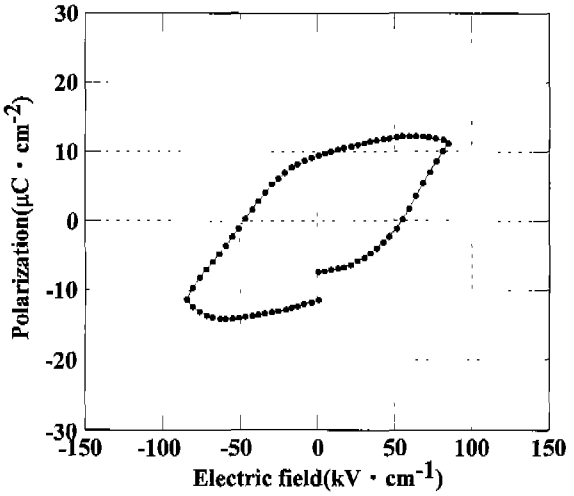

Fig. 3. P-E hysteresis loop of $PbTiO_3$/Pt/MgO film.

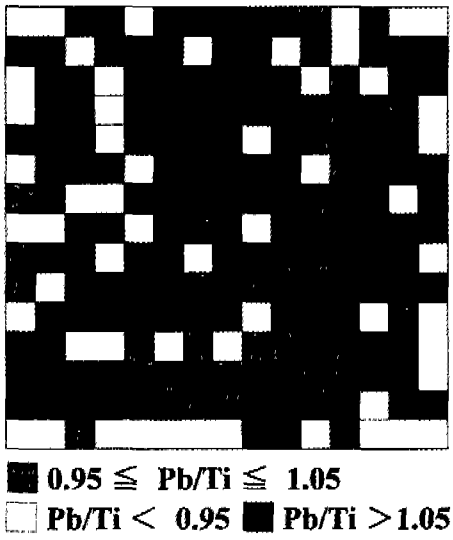

Fig. 4. Schematic diagram of the distribution of composition in thin film.

point using EDS attaching to SEM. The schematic diagram of distribution of composition in annealed film was shown in Fig. 4. It was considered that it was caused because flow and temperature in tail flame of plasma were heterogeneous. The relation between distribution of composition and electric properties were as follows. The relation between composition and remanent polarization was shown in Fig. 5. At stoichiometric composition, Pr showed the lowest value and became gradually large as composition deviated from stoichiometric one. The value of Pr seemed to be large by the influence of leak, but resistivity of points in Fig. 5 were about 10^9 Ω·cm and cocstant, so it was thought that the influence of leak was small. Moreover, H. Madono et al. reported that the value of Pr seemed to be large as the ratio of Pb was high.[10] There was also a possibility that the ratio of Pb influenced the value of Pr. However, it was considered that the greatest reason why the value of Pr became large as composition deviated from stoichiometry was that P-E hysteresis loop did not saturate completely. It was generally known that $PbTiO_3$ was a ferroelectric material that its hysteresis loop was difficult to saturate completely. Therefore, the value of Pr seemed to be changed by composition. The relation between composition and coercive field was shown in Fig. 6. At stoichiometric composition, similarly, Ec showed the lowest value and became gradually large as composition deviated from stoichiometric one. The relation between remanent polarization and coercive field was shown in Fig. 7. It was thought that there was a proportional relation between the value of Pr and Ec and the value of Pr was increasing against the rise of the value of Ec. That is to say, it was obvious that P-E hysteresis loop did not saturate completely. The relation between composition and dielectric constant was shown in Fig. 8. The value of ε_r became gradually large as the ratio of Ti became high. S. K. Streiffer et

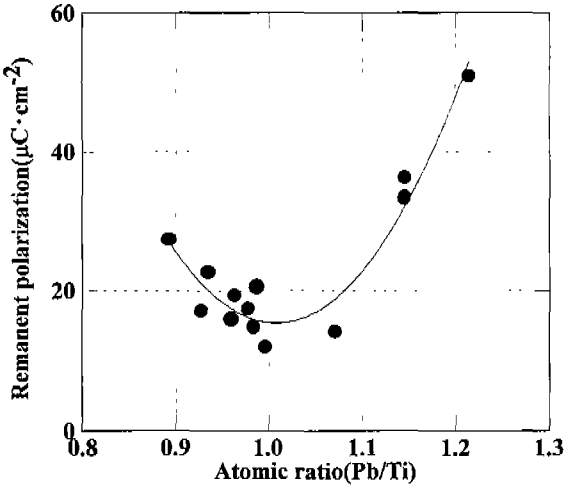

Fig. 5. The effect of composition on remanent polarization of $PbTiO_3$/Pt/MgO film.

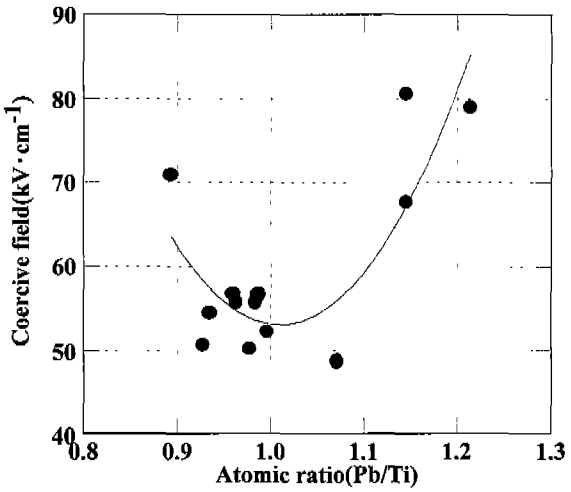

Fig. 6. The effect of composition on coercive field of $PbTiO_3$/Pt/MgO film.

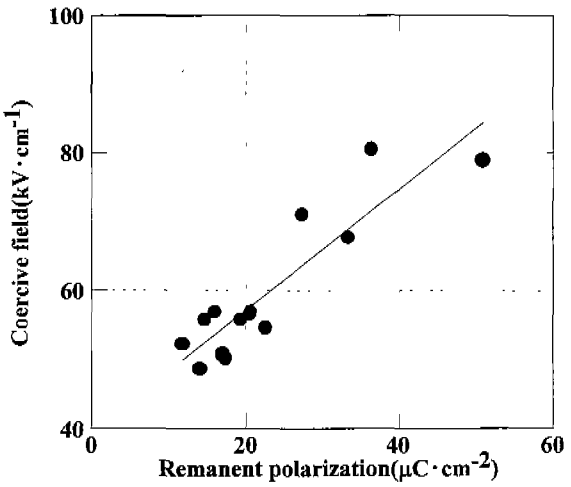

Fig. 7. The relation between remanent polarization and coercive field of $PbTiO_3$/Pt/MgO film.

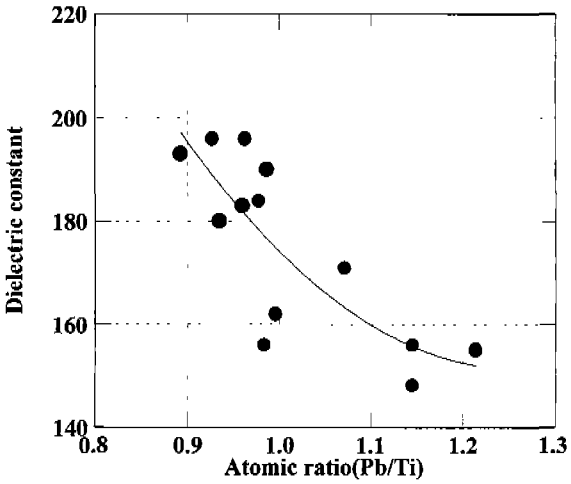

Fig. 8. The effect of composition on dielectric constant of $PbTiO_3$/Pt/MgO film.

al. reported that Curie temperature changed together with the ratio of Ti.[11] On (Ba, Sr)TiO_3 thin film, Curie temperature became high as the ratio of Ti became high, consequently, the value of ε_r became small. On $PbTiO_3$ thin film, on the other hand, the value of ε_r became large as the ratio of Ti became high, but there was a possibility that the ratio of Ti influenced the value of Curie temperature and, as the result, the value of ε_r changed. The relation between composition and loss factor was shown in Fig. 9. At stoichiometric composition, tand showed the highest value and became gradually small as composition deviated from stoichiometric one. It was generally known that the value of ε_r became large in the case that the value of tand was large. The possibility that the ratio of Ti influenced the value of Curie temperature and ε_r became much higher because the value of tand did not become large as the ratio of Ti became high.

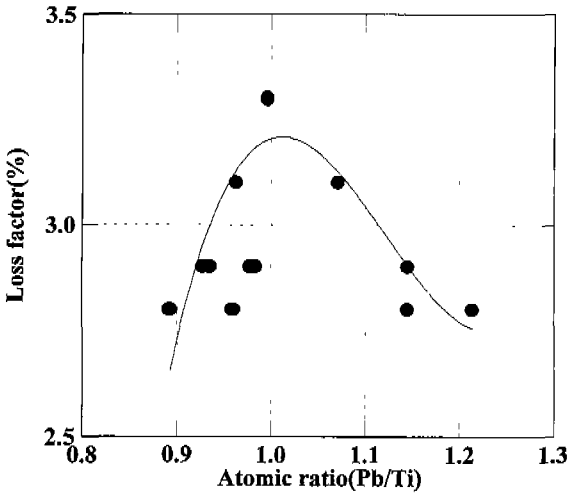

Fig. 9. The effect of composition on loss factor of $PbTiO_3$/Pt/MgO film.

IV. Summary

As-deposited $PbTiO_3$ thin film prepared on (100)Pt/(100)MgO substrate at 1.33×10^4 Pa by low-pressure thermal plasma deposition was grown epitaxially, but was consisted of many rectangular shaped grains, with many grain boundaries and it was impossible to measure electric properties. The degree of crystallization of s-deposited film prepared at 1.00×10^4 Pa was low and as-deposited film was not grown epitaxially, but with high crystallinity and grown epitaxially by after annealing and, consequently, could not be found clear grain boundaries. The value of ε_r, tanδ, Pr and Ec of annealed film were 160, 3.2%, 10.4 $\mu C\cdot cm^{-2}$ and 51.2 $kV\cdot cm^{-1}$, respectively. The distribution of composition in annealed film was found and several relations were found out between composition and electric properties. At stoichiometric composition, Pr and Ec showed the lowest value and became gradually large as composition deviated from stoichiometric one. It was considered that the greatest reason why the value of Pr and Ec became large as composition deviated from stoichiometry was that P-E hysteresis loop did not saturate completely. Moreover, the value of ε_r became gradually large as the ratio of Ti became high. there was a possibility that the ratio of Ti influenced the value of Curie temperature and, as the result, the value of e_r changed.

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