A Study on the Imaging Formation in Ferroelectric Film

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Abstract

In this paper, the preparation of lead zirconium titanate(PZT) thin film by sol-gel processing was described. Thin film coated with thickness of 4 μm on the stainless steel substrates using the multiple spin-coating process.

The crystalline phases of PZT powder and film were investigated by X-ray diffraction pattern and PZT thin film has perovskite structure over the 600℃ annealing temperature.

Corona charging characteristics of the ferroelectric PZT thin film at 600℃ were investigated by electrophotographic measurement.

A difference in the charging characteristics between positive and negative corona charging was found. The charge acceptance depended on the polarity of corona and the poling of film.

According to the D-E hysteresis measurment, PZT thin film can be poled by corona charging without use of top electrode. The remnant polarization in the PZT thin film is generally in the order of 48 $\mu C/cm^2$.

From this results, the ferroelectric PZT thin film will be possible to apply for the add-on type imaging formation.

1. Introduction

Recently, the electrophotography is the most popular technique in high speed image recording systems for reproduction of hardcopy such as copier page printer facsimile and so on.

Ferroelectric material is classified into a sub-group in the dielectric material which have a spontaneous polarization with switching characteristic.

Ferroelectrics such as lead zirconium titanate(PZT), poly vinylidene fluoride(PVDF) and its copolymers have been applied to a wide variety of electronic devices such as transducer, speakers, infrared detecters, etc.[1-3)]

The orientation of dipoles in these ferroelectrics are persistently maintained at temperature below the Curie point. Hence it could be an attractive application to utilize this unique property as the information memory similar to the magnetic memory in magnetic recording systems.

Study of photoconductor with memory effect have been proposed an the image recording system. Recently Date[4)] and Furukawa[5)] tried to apply a copolymer of vinylidene fluoride and trifluoroethylene (PVDF-TrFE) to a digital memory system. It is concerning the application of the ferroelectric polymer film to the information with memory effect which is based on reversing the remnant polarization in ferroelectric polymer films by laser beam irradiation. The readout of the recorded signals was accomplished by probing the pyroelectric current induced by a readout laser beam. The reconstruction of the recorded images were performed by a computer added graphic method. In fact, few application to imaging systems reproducing hardcopy of the recorded image have been proposed so far.

It is a practical and convenient technique for reading out the remnant polarization in the phtoreceptor that has not been developed yet.

In this study, the PZT ferroelectric thin films produced by sol-gel method, which could be application such as an add-on type image recording system and an high memory imaging system.

2. Experiment

2.1. Preparation of films

Figure 1 illustrates the flow diagram for the preparation of stock solution and films using a sol-gel process. Lead acetate trihydrate, zirconium propoxide and titanum

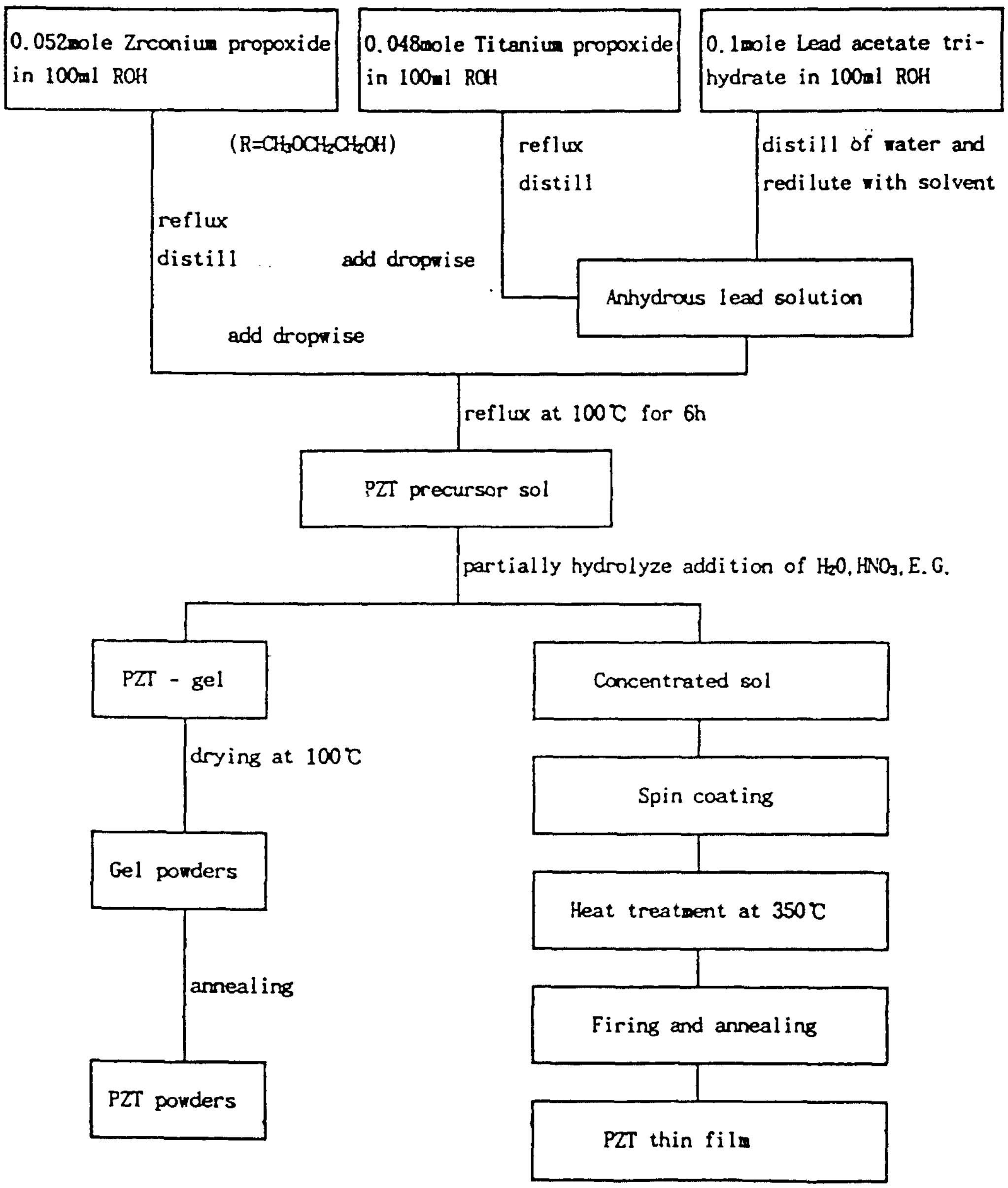

Fig.1 Fabrication process of PZT thin film and powder by sol-gel processing.

propoxide were used as the starting material. Lead acetate trihydrate was dehydrated by boiling with 2-methoxyethanol at 125℃ and cooled to below 80℃. In this solution, zirconium propoxide and titanium propoxide with 2-methoxyethanol were added. After the solution was distilled at 100℃ for 6 hours. Nitric acid was added to the solution which acted as improved the minuteness of film, to controlled the thin film property, we added some water to the solution which accelerated partial hydrolysis. Ethyleneglycol addition prevent a crack in annealing.

2.2. X-ray diffraction measurement

The crystalline phases of PZT powder and thin films were identified by X-ray diffraction(Rigaku, Japan). X-ray(Kα ray) was exposed to sample through nikel filter. Width of X-ray was 0.01° , scanning speed was 4° /min, accelerating voltage was 30kV, current was 15mA, diffusion anglur range (2θ) was 20 - 60° .

2.3. Corona charging charactristic measurement

Poling of ferroelectric thin film was accomplised by the following two method;

① Applying high electric bias with a conductive substrate and a gold electrode which was deposited on to the sample surface in advance.

② Exposing the corona to the free surface of the sample.

In applying the ferroelectric thin film to image recording system which reguires a large area and its uniformity in terms of properties, uniform poling of the thin film was necessary in a large area in addition to a non-electrode process.[6,7] Figure 2 illustrates a schematic diagram of corona charging experiment.

2.4. D-E hysteresis measurement

Figure 3 illustrates a schematic diagram of Sawyer-Tower circuit. It was utilized to confirm the D-E hysteresis characteristics and poling level. A frequency was 60Hz, reference electrostatic capacity was 0.24 μF, applied vortage was ± 8kV, poling time was 20 min.

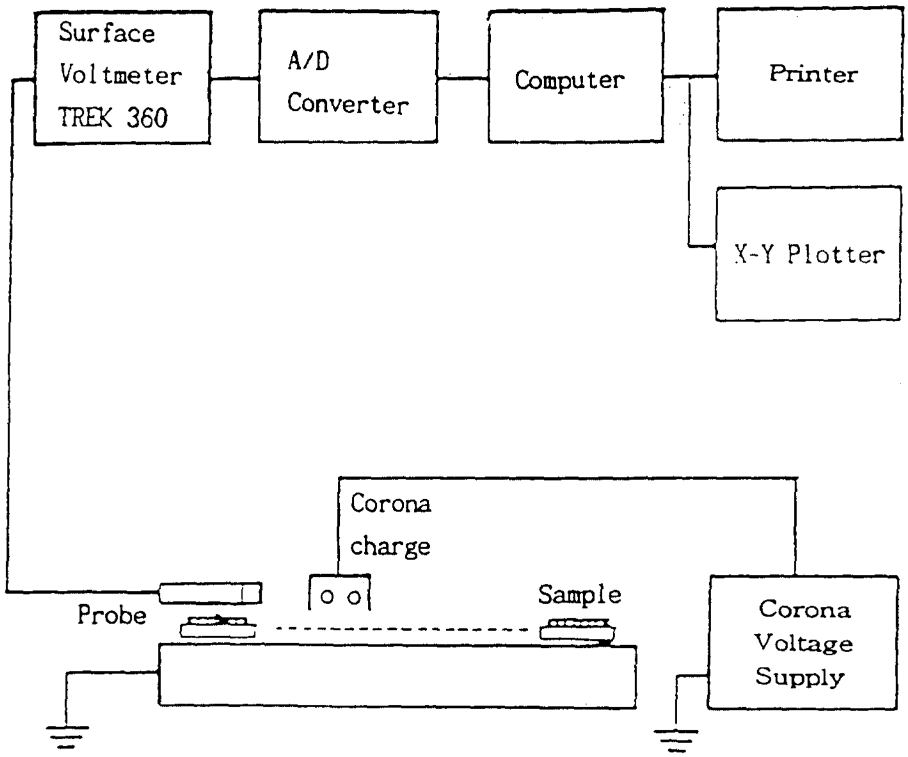

Fig.2 Schematic diagram of apparatus for corona charging.

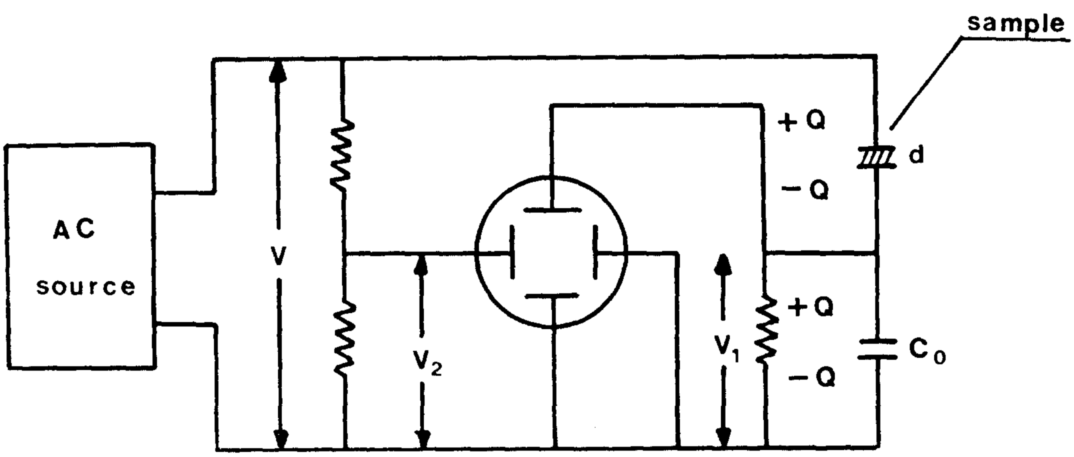

Fig. 3 Schematic diagram of Sawyer-Tower circuit.[8)]

3. Results and Discussion

3.1. X-ray diffraction characteristics

Figure 4 illustrates X-ray diffraction patterns for PZT powder, annealing 500 to 700 ℃ by sol-gel process. The sample with at 500℃ for 30min shows partially to beginning crystalization from small peak of 32° . The sample with at 550℃ for 30min shows to some degree of crystalization was progressed from peak of 32° but it was pyrochlore phase from wide and small peak of 29° . Above 600℃, it shows perovskite phase.

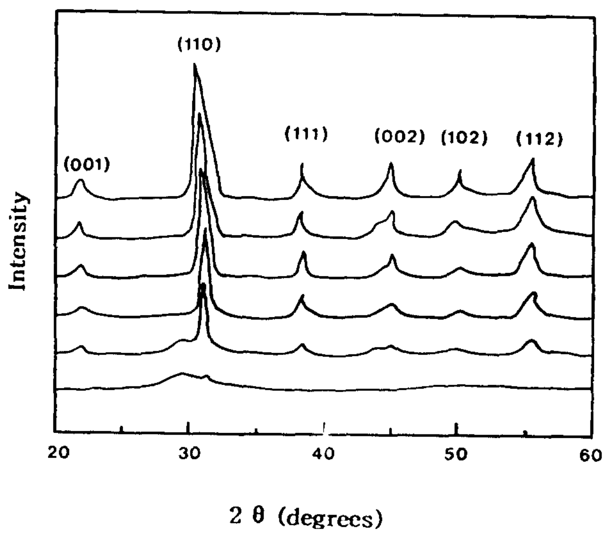

Fig. 4 X-ray diffraction patterns for PZT powders at various temperatures.

Figure 5 illustrates X-ray diffraction pattern of PZT thin film on stainless steel with 4μm thickness at 600℃ annealing. This X-ray diffraction pattern was similer to the sample at 600℃ annealing powder, which shows large peak of 32° . In this results indicated that ferroelectric PZT was perovskite phase when annealing temperature was 600℃ above.

Hance, the films annealed at 600℃ were used for in this study.

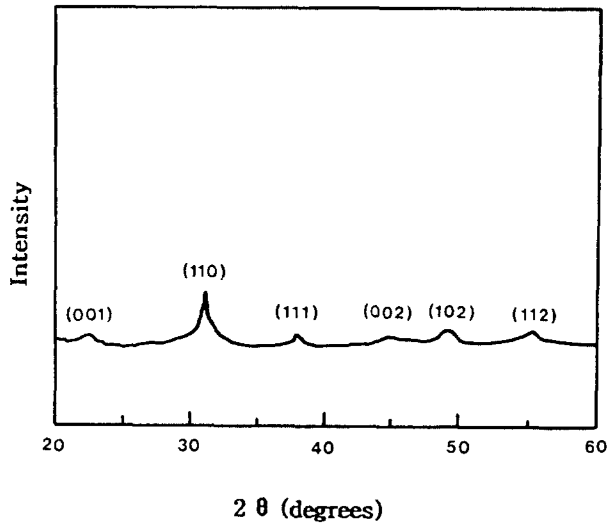

Fig. 5 X-ray diffraction pattern for PZT film on stainless steel at 600℃annealing.

3.2. Corona charging characteristics

Corona charging characteristics of PZT thin films were investigated for negative and positive coronas. Figure 6 shows the characteristics of corona charging for a typical insulator film, polyester. In polyester film, surface potential was saturated at initial corona charging which was unchanged according to increase of time.

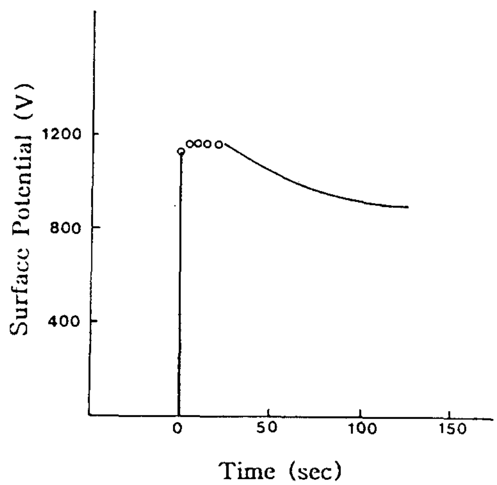

Fig. 6 The behavior of charging and surface potential for polyester.

Negative and Positive Corona charging characteristics of ferroelectric PZT thin films at 600℃ annealing were shown figure 7 and 8, respectively. It was different with polyester film. Ferroelectric PZT thin film was saturated according to increase of time. In figures, solid circles shows poled film and open circles shows unpoled film. Poling condition was voltage of DC-8kV applied through corona wire for 20 min and then surface potential was allowed to decay to 0(V) in several minutes. For negative corona charging, initial potential was measured -130V, which was similar to poled and unpoled film. Saturation potential was in unpoled film was -370V and poled film was -260V.

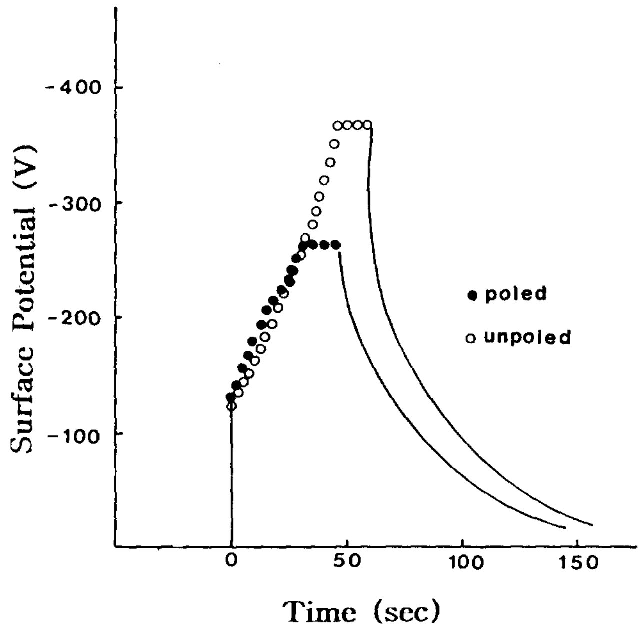

Fig. 7 The behavior of charging and surface potential of PZT at 600℃ annealing with negative pulse corona.

For positive corona charging, initial potential was in unpoled film was 435V and poled film was 331V. It was different to negative corona charging. This is quite different from corona charging characteristics of conventional dielectrics.

Surface potential on the PZT thin film increased slowly for negative charging, while it increased much faster for positive charging.

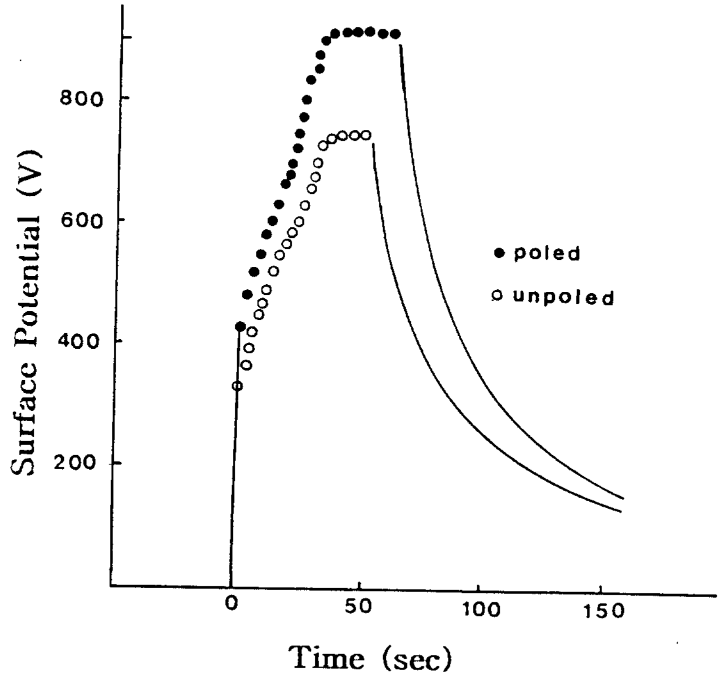

Fig. 8 The behavior of charging and surface potential of PZT at 600℃ annealing with positive pulse corona.

The difference between not only negative and positive but also poled and unpoled films were observed. The difference of charge acceptance was considered that for unpoled film, it was occured carrier injection from interface of substrate, for poled film, it was occured hole injection from substrate in negative corona charging and bulk conductivity in positive corona charging.

These results indicate that corona charging characteristics of PZT thin films were strongly depended on the polarity of the corona.

3.3. D-E hysteresis characteristics

Figure 9 shows D-E hysteresis curve of ferroelectric PZT thin films at 600℃ for 30 min annealing. It shows typical hysteresis curve of PZT thin film by sol-gel process.

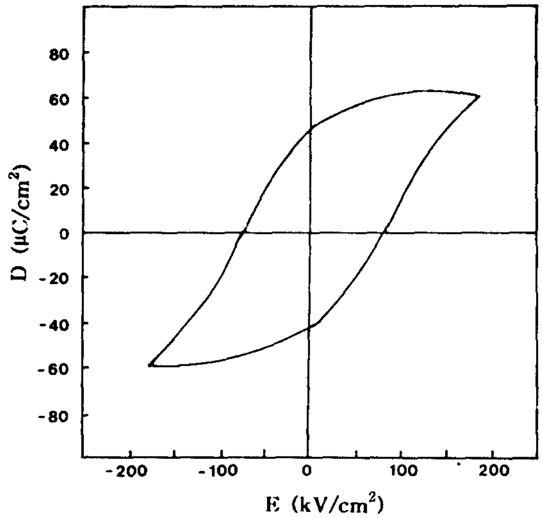

Fig. 9 D-E hysteresis curve for PZT film at 600℃ annealing.

Figure 10, 11 shows D-E hysteresis curves of poled PZT thin films with negative and positive corona charging, respectively.

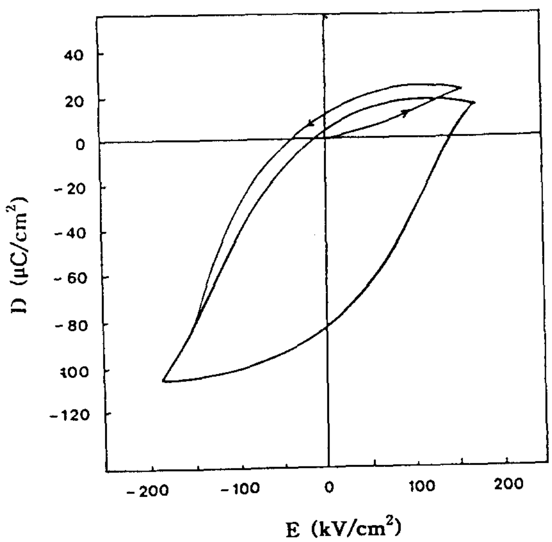

Fig. 10 D-E hysteresis curve for PZT film poled by negative corona.

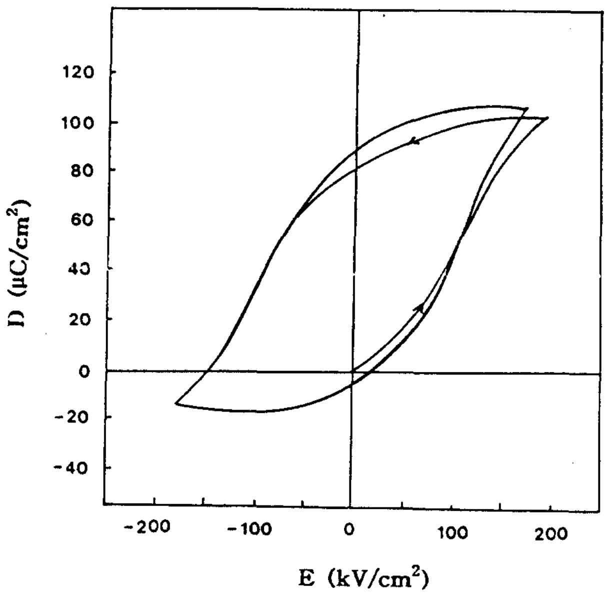

Fig. 11 D-E hysteresis curve for PZT film poled by positive corona.

As we can see from these figures, ferroelectric PZT thin film can be poled by either positive or negative corona charging and also can be reversed under an opposite polarity to that for poling. Therefore we can poling the ferroelectric PZT thin film by corona charging without top electrode.

Figure 12, 13 shows the plots of surface potential and the remnant polarization vs the poling time for negative and positive corona charging, respectively. For negative corona charging, according to increase of charging time to 4, 8, 12 and 16 min, surface potentials increase to be -60, -100, -150 and -170V, remnant polarizations increase to be 30, 70 and 80 $\mu C/cm^2$, respectively. For positive corona charging, according to increase of charging time to 2, 4, 6 and 8 min, surface potentials increased to be 100, 190 and 210V, remnant polarizations increase to be 35, 65, 80 and 85 $\mu C/cm^2$, respectively.

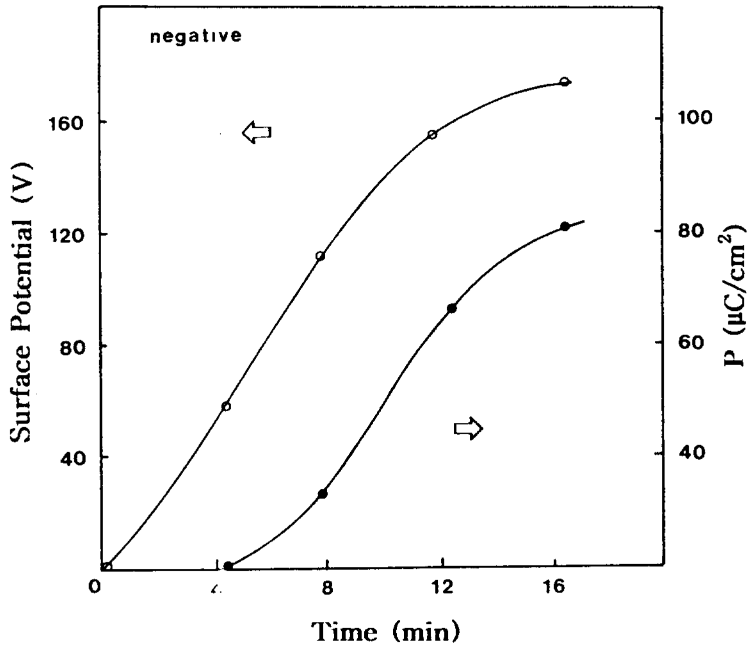

Fig. 12 Time dependence of surface potential and the remnant polarization for PZT film charged by negative corona.

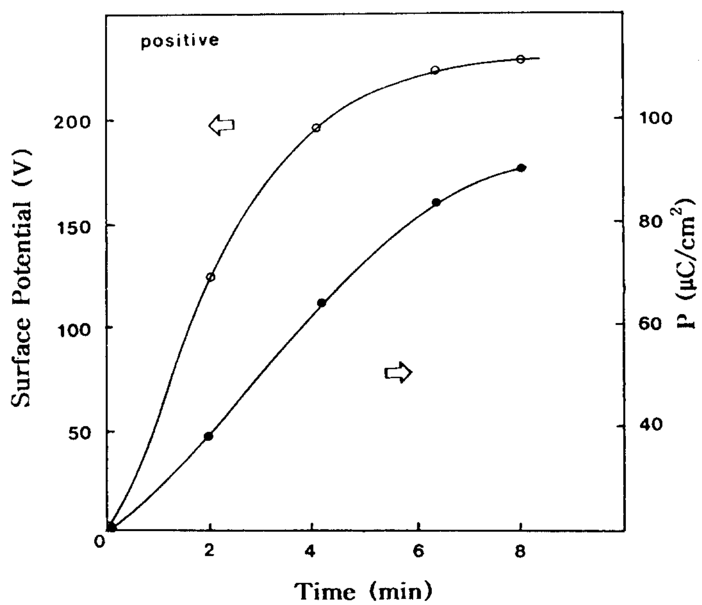

Fig. 13 Time dependence of surface potential and the remnant polarization for PZT film charged by positive corona.

The poling level depends on the surface potential of PZT thin film during corona charging. In this results, imaging formation system can be considered as follows;[9]

1) Poling by corona
2) Image recording with thermal pulse
3) Corona charging
4) Development
5) Transfer

Ferroelectric PZT thin film is applicable to image recording system with memory effect and high image quality.

4. Conclusions

In this study, the preparation of PZT thin film by sol-gel processing, X-ray diffraction, corona charging and D-E hysteresis were described. Ferroelectric PZT thin film was perovskite phase over 600℃ annealing temperature. PZT thin film was poled with corona charging without top electrode. It is possible to be applied for the add-on type image recording system.

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