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ARTICLE

Piezoelectricity of ZnO Films Prepared by Sol-Gel Method†

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ZnO piezoelectric thin films were prepared on crystal substrate Si(111) by sol-gel technology, then characterized by scanning electron microscopy, X-ray diffraction and atomic force microscopy (AFM). The ZnO films characterized by X-ray diffraction are highly oriented in (002) direction with the growing of the film thickness. The morphologies, roughness and grain size of ZnO film investigated by AFM show that roughness and grain size of ZnO piezoelectric films decrease with the increase of the film thickness. The roughness dimension is 2.188-0.914 nm. The piezoelectric coefficient d_{33} was investigated with a piezo-response force microscope (PFM). The results show that the piezoelectric coefficient increases with the increase of thickness and (002) orientation. When the force reference is close to surface roughness of the films, the piezoelectric coefficient measured is inaccurate and fluctuates in a large range, but when the force reference is big, the piezoelectric coefficient d_{33} changes little and ultimately keeps constant at a low frequency.

Key words: ZnO thin films, Piezoelectric coefficient, Piezo-response force microscope, Sol-gel, Surface roughness

I. INTRODUCTION

ZnO piezoelectric thin film is a very useful multifunction semiconductive material and is widely used in piezoelectric, transparent conducting electrodes, optoelectric devices, and gas sensors because of their excellent characteristics. It is also attractive for high frequency surface acoustic wave device application [1]. ZnO is a novel wide direct-gap semiconductor with an energy gap of 3.3 eV and a high free exciton binding energy of 60 meV at room temperature which has great usages in information age. There has been great progress in the science of piezoelectricity and its applications have mushroomed in many fields, such as medicine, military affairs, computers and telecommunications. ZnO has recently become a very fashionable material due to its applications generated by particular properties [2]. Its high piezoelectricity coefficient and electromechanical coupling factor have led to substantial research into the origin of its strong piezoelectricity and applications. Piezoelectric characterization of individual ZnO nanobelt has been investigated by piezo-response force microscope (PFM) [3]. In that work, the effective piezoelectric coefficient d_{33} of ZnO nanobelt was found to be frequency dependent and much larger than that of the bulk (0001) ZnO, which support the application of ZnO nanobelts as nanosensors and nanoactuators.

The piezoelectric coefficient and resistivity of sputtered ZnO films undoped and doped with Cu, Ni, Co, and Fe have been investigated and the results indicated that Cu dopant can enhance the *c*-axis orientation and the piezoelectric coefficient (d_{33}) which is promising to fabricate the ZnO films doped with Cu for SAW device applications [4]. In general, ZnO films prepared by many methods did not have good performance and there would always be too large a roughness or big particles on the film surface. Especially, roughness on the films surface can play an important role in micro/nano sensors or actuators. Recently in the study of ZnO piezoelectric films, many researchers have been concerned with the preparation techniques and characterization, but few reports discuss the effect of roughness on the piezoelectric films. In this work, the piezoelectric characterization and the effect of different roughnesses on ZnO piezoelectric films were discussed in detail.

Recently various ZnO semiconductor nanostructures have been fabricated, such as an oriented structure of ZnO nanorods and ZnO nanowires [5]. ZnO thin films can be obtained by different methods (sol-gel technique, chemical vapour deposition (CVD), pulse laser deposition (PLD), spray pyrolysis, magnetron sputtering, etc.). Sol-gel technique have many advantages in preparing ZnO films, such as strong *c*-axis orientation, ease of compositional modifications, large films, simplicity of working principle, low cost, and low annealing temperature. The sol-gel method is therefore prevalent today and ideal for exploratory research.

When an electric field is applied to a piezoelectric material, it strains due to the converse piezoelectric effect. In ideal PFM piezoelectric measurement, an electric field is applied to a piezoelectric material, and the

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tip accurately follows the piezoelectric motion. Since the piezoelectric constant represents the linear relation between the strain and applied field, the piezoelectric motion will also be of the frequency at which the piezoelectric is driven by a voltage. These small piezoelectric displacements can be measured in several techniques, including PFM. Piezoelectric measurements of ZnO piezoelectric films were performed in contact mode with a PFM. PFM has become a useful characterization technique and has been described in several books [6-8] and in the literatures [3,4]. The PFM technique has the advantage of being able to measure the piezoelectric effect at single points on a sample. In this configuration, it is more difficult to accurately determine the electric field, but the measurements can be performed readily and directly upon the ZnO piezoelectric thin film. The PFM technique measuring the absolute magnitude of the effective longitudinal d_{33} is based on the detection of vibrations of ZnO piezoelectric films and a laser and position sensitive photodetector (PSPD) combination which can detect the cantilever deflection. The conductive tip that supplies current to the film and also measures the piezoelectric motion due to the inverse piezoelectric effect is made by coating Rh and the tip radius is about 10 nm. The input signal is in the range of 1-5 V, and the vertical deflection signal A_0 of the cantilever is recorded by a lock-in amplifier. The slope of the amplitude versus the input signal U_0 gives d_{33}.

II. EXPERIMENTS

The piezoelectricity of ZnO films prepared by sol-gel with different thickness and roughness is a key characteristic for the piezoelectric measurement. The ZnO piezoelectric films were deposited on Si(111) wafer substrates by the sol-gel process. Sol was prepared by dissolving zinc acetate (ZnAc) (99% purity) in 2-methoxyethanol and MEA (1:1:1 in mol). MEA and 2-methoxyethanol were used as stabilizer and solvent, respectively. The mixture was confected to 0.35 mol/L and stirred ultrasonically. A magnetic stirrer was used at 55 °C for 60 min till a clear solution was formed which was found to be stable and transparent with no precipitate or turbidity after cooling to room temperature. The coating was made 48 h after the sol was prepared in the room temperature in order to make it more glutinous. The single-crystalline Si(111) substrates were degreased in the mixture of acetone and tetrachloride carbon (1:1 in volume) and stirred ultrasonically for 30 min, and then washed 10 times by distilled water, and in the end dehydrated by alcohol many times. Before coating, substrates were dipped in HF solution (5%) for 10 s, washed by distilled water completely, and then dehydrated by alcohol standby. The sol was dripped onto Si(111) substrate and then the substrate was spin-coated with the sol at a speed of 3200 r/min for 40 s in air. After each coating on the substrate, the substrate coated with ZnO film layer was dried at 100 °C for 5 min over a hot plate in air. Then the deposited ZnO film was annealed in air at a temperature of 500 °C for 1 h to complete one cycle of crystallization of the film. This process of coating and subsequent heat treatment was repeated seven times in order to get thicker ZnO films.

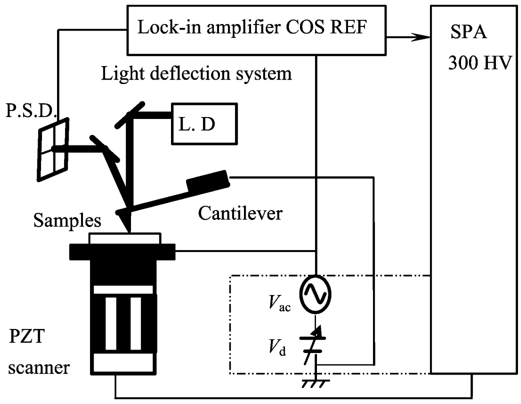

FIG. 1 Schematic diagram of experiments for piezoelectric measurements.

The thickness of the ZnO film was built up by increasing the number of coatings (1-7 coating cycles). The thickness of each ZnO film was measured by a scanning electronic microscope (SEM) which was also used to illustrate the formation of crystallites on the ZnO film surface. X-ray diffraction (XRD) was used for structural characterization and phase identification of ZnO films using Cu Kα radiation operating at 40 kV, 150 mA. The surface morphology and roughness of the deposited ZnO films was investigated using AFM. Piezoelectric coefficient d_{33} measurements of the series of films with different roughness were performed with a PFM (Seiko SPA300HV) in contact mode. A schematic diagram of piezoelectric measurement system is shown in Fig.1. The function generator drives the ZnO thin film piezoelectric capacitor, and in the experiments the frequency varies from 200 Hz up to 1 kHz which is beyond most environmental noise frequencies and well below the tip resonances. The peak-to-peak potential varies up to 5 V. The frequency and the applied voltage are stepped through computer control, and the lock-in amplifier records the PFM tip displacement at the frequency. From the slope of the resulting displacement *vs.* applied voltage plot, we can calculate the piezoelectric constant. Measurements were performed on ZnO piezoelectric thin films with different thickness, frequency and voltage.

III. RESULTS AND DISCUSSION

A. Microstructure of ZnO piezoelectric films

The structural properties and the cross-section of ZnO films were investigated by XRD and SEM as shown

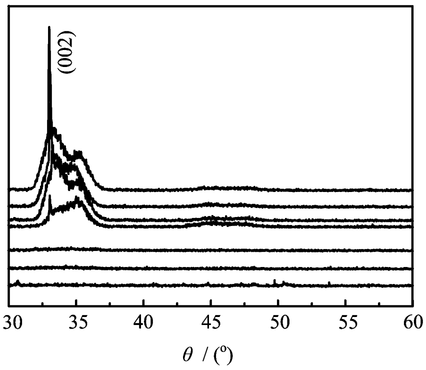

FIG. 2 XRD pattern of the thin ZnO films with seven different thickness of 20, 30, 53, 62, 70, 80, and 88 nm from bottom to top.

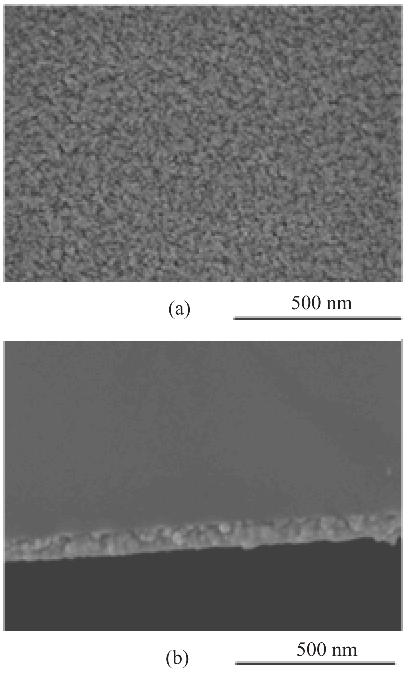

FIG. 3 Surface SEM image (a) and cross-section SEM image (b) of the deposited ZnO film with thickness of 88 nm.

in Figs. 2, 3, and 4. Figure 2 shows the XRD patterns of ZnO piezoelectric films with thickness of 20, 30, 53, 62, 70, 80, and 88 nm, respectively. From the figure we can see that as the film thickness increases from 20 nm to 88 nm which is polycrystalline with wurtzite structure, the intensity of (002) peak (c-axis orientation) increases, which implies an improvement in the crystalline quality of the film. The SEM micrographs of ZnO films with seven different thicknesses showed uniform tightly packed grains whose size decreases with the increase in thickness. The surface and cross-sectional SEM image of film with a thickness of 80 nm grown on Si(111) by sol-gel was shown in Fig.3.

In Fig.2, the (002) peak of thin films moves to a small angle and are fat compared with thick ZnO films (>100 nm) in the literature. The reason may be that the films are very thin and in the ZnO thin films stress exists after annealing. The lattice parameters were calculated using the observed values of 2θ for (002) plane and (101) plane and the d-values (inter-planar spacing) for the hexagonal structure, which is given by

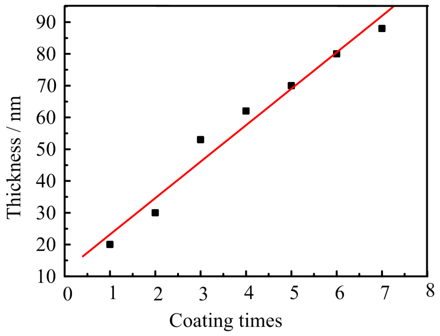

FIG. 4 The thickness of the films at different coating times.

$$\frac{1}{d^2}=\frac{4\left(h^2+hk+k^2\right)}{3a^2}+\frac{l^2}{c^2} \tag{1}$$

where d is inter-planer spacing, a and c are base vectors of hexangular lattice, h, k, l are exponential of crystal surface. As to ZnO(002), h=k=0, l=2, hence c=2d. Since $2\delta\sin\theta=nl$, when n=1, the lattice parameter of ZnO film was calculated using the observed values of 2θ for (002) plane, which is given by

$$c=\frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3(a/c)^2}(h^2+hk+k^2)+l^2} \tag{2}$$

where λ, θ are wavelength of X-ray (0.15418 nm) and angle of diffraction, respectively. The lattice parameter of ZnO film calculated is a little bigger than that of ZnO bulk (0.521 nm). Because tensile stress exists in the ZnO film at c-axis orientation, which makes the lattice parameter become bigger and diffractive apex move to a small angle.

According to Wu *et al.* [9] and Chen *et al.* [10], a film with a smooth surface which is well-oriented by X-ray analysis exhibits a high effective SAW coupling factor, while a rough surface will enlarge the insertion loss of the SAW device. For ZnO piezoelectric film, the surface smoothness is a critical characteristic of piezoelectric material for the fabrication of low loss piezoelectric devices and high frequency surface acoustic wave device application.

To study the effect of roughness against piezoelectric coefficient d_{33}, the samples prepared by sol-gel were investigated by AFM. The results indicated that the ZnO films have a smooth surface with the roughness from 2.188 nm to 0.914 nm. Figure 5 illustrates the typical AFM morphologies of ZnO films grown on Si(111) with different thickness. As shown in the figure, the surface of the ZnO thicker film was smoother than the thinner.

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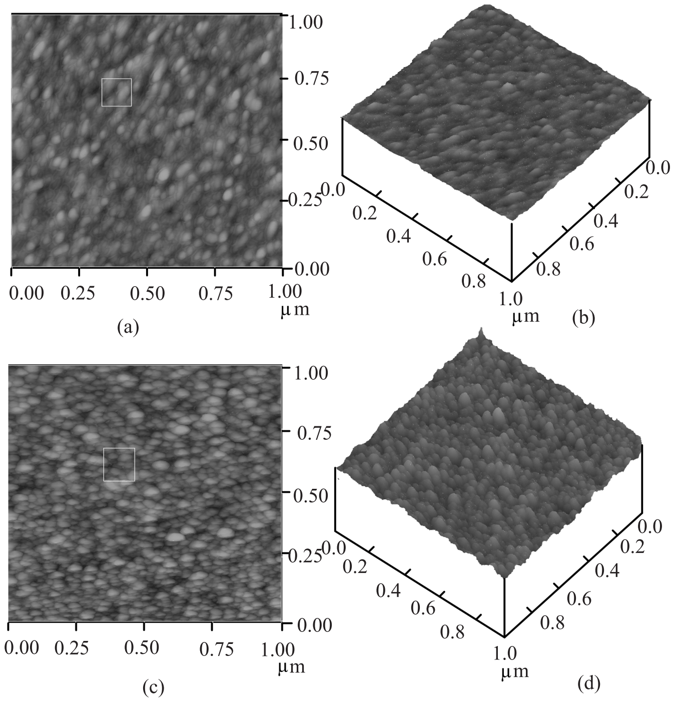

FIG. 5 (a) and (c) AFM images and roughness analysis of the ZnO film with thickness of 20 and 30 nm, respectively; (b) and (d) three-dimensional image of ZnO films.

The average surface roughness (R_a) of ZnO films at different thickness of 20, 30, 53, 62, 70, 80, and 88 nm was 2.188, 1.892, 1.891, 1.291, 1.245, 1.015, and 0.914, respectively. The grain becomes denser with the increase in thickness.

B. Piezoelectric properties of ZnO films

PFM is becoming a standard method for the study of piezoelectric phenomena [3,4]. The piezoelectric properties of ZnO films with smooth and rough surfaces were measured using the PFM technique in contact mode. The sample first was located on the sample platform with silver cataplasm, then the sample with silver cataplasm was heated for 60 min in a heater at a temperature of 100 °C. A conductive tip coated with Rh was used as a top electrode (0 V) which can obtain the z-deflection signal.

An ac signal is applied between the grounded tip electrode and the substrate electrode. When the electric field is applied to a piezoelectric ZnO film, it strains due to the converse piezoelectric effect. The tip perpendicular displacement is sensed by the photo-sensitive detector and its output signal is split into amplitude and phase by a lock-in amplifier. The ac signal was employed with a frequency of 0.5 kHz, and the peak-to-peak potential varied up to 5 V. The 0.5 kHz frequency is below the tip resonances and above most environmental noise whose frequency range is 20-200 Hz. In the piezoelectric measurement experiments, we changed the frequency from 200 Hz to 1 kHz and amplitude of voltage which is stepped through computer control. Also, we changed the depth of the tip's penetration into the ZnO films so as to research the relation between the piezoelectric coefficient and roughness. The displacement of cantilever at the frequency ω and amplitude of voltage A is recorded by a lock-in amplifier. The piezoelectric coefficient d_{33} can be calculated from the slope of the resulting amplitude of displacement *vs.* that of applied voltage plot, which are both peak-to-peak values of displacement and applied voltage, respectively. The piezoelectric coefficient d_{33} is calculated by [3,11]

$$d_{33} = A_0/U_0 \tag{3}$$

where A_0 is vibration amplitude, U_0 is the amplitude of the testing ac voltage.

Piezoelectric measurements were performed on seven types of thin ZnO films with seven types of thickness and roughness, and also on Si substrate with no film. Figure 6 shows piezoelectric measurements of ZnO thin film (20 nm in thickness) and single-crystalline Si(111). Piezoelectric constants for the measurements were d_{33}=5.81 pm/V and d=0.26 pm/V. The single-crystalline Si measurement is at our experimental noise level (<0.5 pm/V). In all the piezoelectric measurement, the interaction between the tip and electric field present was ignored [11].

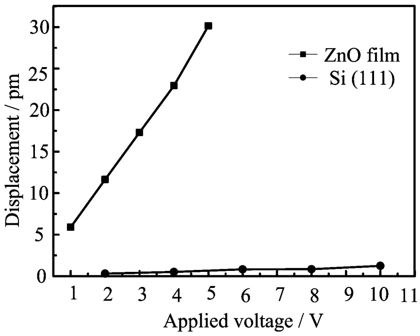

FIG. 6 Piezoelectric measurements of thin film ZnO with thickness of 20 nm and single-crystalline Si (111). Piezoelectric coefficient of the samples for the measurements were d_{33}=5.81 pm/V and d=0.26 pm/V while the experimental noise level was 0.5 pm/V.

Figure 7 is piezoelectric measurements of varies thickness ZnO thin films. As the figure shown, the piezoelectric coefficient d_{33} is size-dependent from 5.81-28.7 pm/V, which is bigger than that of the bulk (0001) ZnO (9.93 pm/V) in the strong c-axis orientation. From the result of measurements, when the ZnO thin films are not strong c-axis orientation, the piezoelectric coefficient d_{33} is close to that of the bulk. When the films are approaching strong c-axis orientation, d_{33} is increasing rapidly. Therefore, the piezoelectric coefficient d_{33} increases with increasing thickness size.

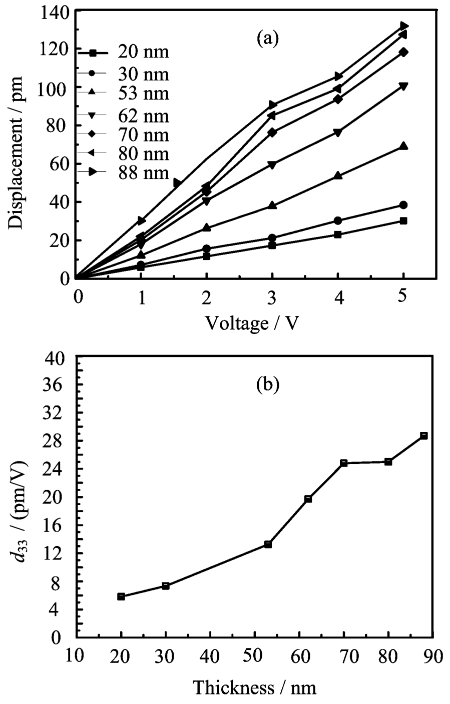

FIG. 7 (a) Piezoelectric measurements of seven ZnO thin piezoelectric films: size-dependence of piezoelectric coefficient d_{33}. Each value in the figure is the average of 10 points measurement and each point is performed at an applied voltage amplitude from 1 V to 5 V with frequency of 500 Hz. (b) the trend of d_{33} intuitionisticly.

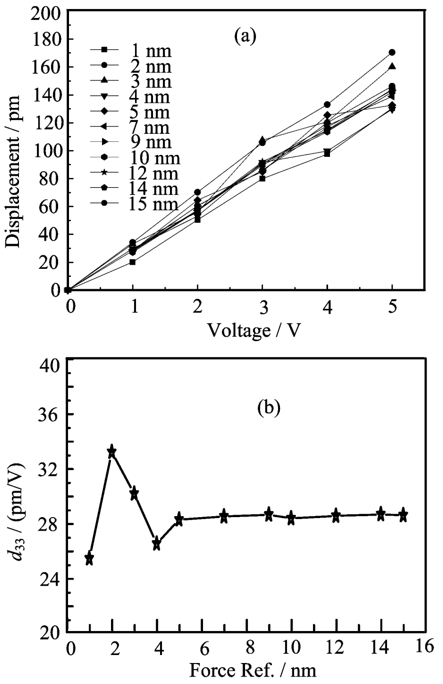

FIG. 8 (a)Piezoelectric measurements of the thin ZnO film (88 nm thick) with Force Ref. from 1-15 nm. The piezoelectric constant d_{33} fluctuates greatly owing to the loose contact between the tip and the film surface which were both vibrating with a frequency. (b) shows the trend of d_{33} intuitionisticly.

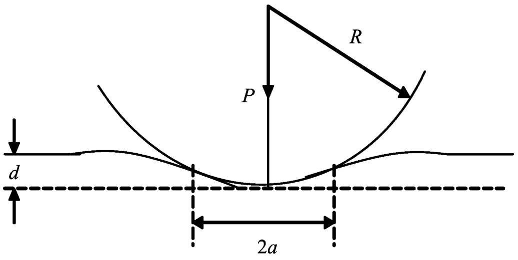

FIG. 9 The Hertz model.

Since the ZnO thin films is not absolutely smooth which were very rough against the thickness in nanoscale. Figure 8 shows that when the thickness of the film was 88 nm, the piezoelectric constant d_{33} fluctuated greatly owing to the loose contact between the tip and the film surface which were both vibrating with a frequency ω. Force Reference (Force Ref.) must be negative, the approach will not work properly if it is positive. The value of the x-coordinate in the Fig.8 is the absolute value of the Force Ref. The AFM tip radius is about 25 nm while the top electrode is the small area where the tip was in contact with the thin film. To calculate the depth of the tip's penetration into the film, we use the Hertz model (Fig.9), in which the tip is regarded as a sphere and the film as an infinity plane. In the modeling, the radius and the elastic modulus of the tip are R and E_1, respectively; the elastic modulus of ZnO film is E_2; the Poisson's ratios of the tip and the film are λ_1 and λ_2, respectively. According to Hertz contact theory, the radius of contact area is:

$$a^3 = RP/K \tag{4}$$

$$K = \frac{4}{3}\left[\frac{(1-\lambda_1^2)}{E_1} + \frac{(1-\lambda_2^2)}{E_2}\right]^{-1} \tag{5}$$

The depth of compression is calculated by formula below (E_1=60 GPa, λ_1=0.3; E_2=300 GPa, λ_2=0.24; R=10 nm; P≈20 nN).

$$\delta = a^2/R \tag{6}$$

When the Force Ref. reaches 4 nm, the depth of the tip into the film is about δ=1.335 nm, which is a little bigger than the roughness (0.914 nm) of the film. As the depth of the tip into the film is the same magnitude as the roughness of the film, the effective coefficient does not fluctuate greatly. Thus, microscopic variation and the approach of the piezoelectric film will affect the electrode quality. As to (002) ZnO nanobelt, Zhao *et al.* found that the effective piezoelectric coefficient d_{33} is frequency dependent and is decreasing with increasing frequency which is high [3]. Here, piezoelectric measurements were performed at a low frequency (200 Hz-1 kHz) on ZnO thin film. In generally, the frequency of

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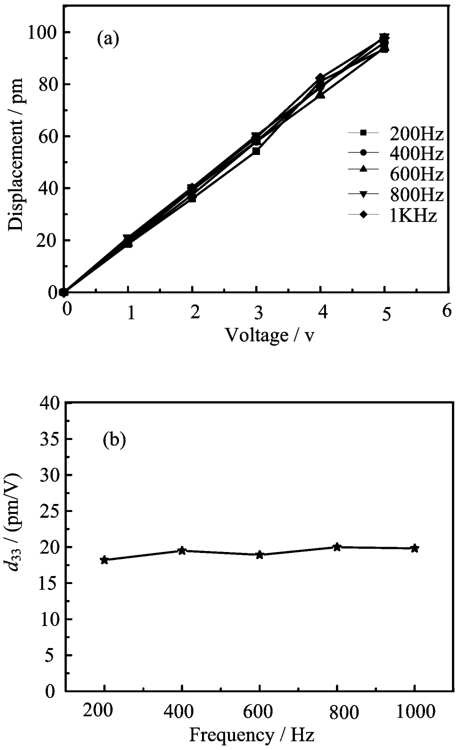

FIG. 10 (a) The ZnO film (62 nm thick) piezoelectric measurements at a low frequency from 200 Hz to 1 kHz. The d_{33} changes little and ultimately keeps constant. (b) The trend of d_{33}.

noise is below 200 Hz, and 1 kHz is the upper limit frequency put by the AFM. Figure 10 shows that at a low frequency, the piezoelectric coefficient of ZnO thin film is not frequency dependent and ultimately keeps constant which does not conflict with the result of Zhao *et al.* measured at a high frequency (~100 kHz).

IV. CONCLUSION

A series of ZnO piezoelectric thin films on single-crystalline Si(111) substrate were prepared by sol-gel technique. The characterization of the films was investigated by AFM, SEM and XRD. The piezoelectric measurements were performed using PFM. When the thickness of the ZnO films is below 100 nm, the piezoelectric coefficient increases with the increasing thickness due to the strong *c*-axis orientation. When the Force Ref. is big enough to ensure the contact between the tip and the film, the value measured is trustworthy, otherwise the value of piezoelectric coefficient fluctuates greatly. The results of piezoelectric measurements reveal that the piezoelectric coefficient of ZnO film is not frequency dependent at a low frequency, but is high frequency dependent.

V. ACKNOWLEDGMENTS

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