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Physica B 373 (2006) 313–316
PHYSICA B
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Characteristics of heterojunctions of amorphous $LaAlO_{2.73}$ on Si

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Received 16 November 2005; received in revised form 2 December 2005; accepted 5 December 2005

Abstract

High-quality heterojunctions consisting of n-type amorphous $LaAlO_{3-\delta}$ and p-type Si without Si interfacial layer were prepared using a thin film deposition system normally used for laser-molecular beam epitaxy. Good *I–V* rectifying property, ferroelectricity of interface enhancement and fast photovoltaic effect have been observed in the $LaAlO_{3-\delta}$/Si p–n heterojunctions. We expect that the multifunctional properties of rectification, ferroelectricity and photovoltaic effect should open up new possibilities in device development and other applications.

PACS: 85.30.Kk; 72.15.Cz; 77.80.−e; 84.60.Jt

Keywords: $LaAlO_{3-\delta}$ and Si; p–n heterojunction; Electric properties; Ferroelectricity; Photovoltaic effect

1. Introduction

Perovskite oxide materials have received general attention because of their remarkable dielectric, piezoelectric, ferroelectric, optical, pyroelectric, electro-optic, superconducting, and ferromagnetic properties. A number of studies have been dedicated recently to exploring the quantum functional properties and verifying new device innovations based on perovskite oxides. The functional properties of rectification and magnetoresistance as well as photoelectricity in epitaxial oxide heterojunctions have been reported [1–3]. Up to now, there have been no reports on the multifunctional characteristics of the heterojunction of amorphous oxide and Si. $LaAlO_3$ has been chosen not only as the substrate for microwave applications due to its low dielectric constant and low loss tangent [4], but also as one of the most promising high-*k* gate dielectric materials due to its dielectric constant of ~24, wide energy band gap of ~6.2 eV and eminent thermal stability [5]. We have reported the high-quality amorphous $LaAlO_3$ thin films grown on Si substrate without SiO_2 interfacial layer [6] and the characteristics of $LaAlO_3$/Si deposited under different oxygen pressure [7]. The amorphous $LaAlO_3$ thin films deposited under lower oxygen pressure exhibit n-type semiconductor behavior owing to the existence of oxygen vacancies [7]. Therefore, the $LaAlO_{3-\delta}$/Si forms a p–n heterojunction. In this paper, we report the multifunctional properties, including electric rectification, ferroelectricity and photovoltaic effect of amorphous $LaAlO_{3-\delta}$ and Si p–n heterojunctions.

2. Experimental

In order to prevent the formation of the SiO_2 interface layer, as mentioned in our previous work [6], we used the two-step method to grow the amorphous $LaAlO_{3-\delta}$ thin film on p-Si substrate. The $LaAlO_{3-\delta}$ thin films were prepared directly on Si (1 0 0) substrates using a thin film deposition system normally used for laser-molecular beam epitaxy (laser-MBE). The initial deposition of about 0.8 nm $LaAlO_3$ layer was carried out at the oxygen pressure 6×10^{-5} Pa and the substrate temperature 350 °C. Then the oxygen pressure was raised to 2×10^{-4} Pa and the substrate temperature raised to 680 °C during deposition. The

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doi:10.1016/j.physb.2005.12.038

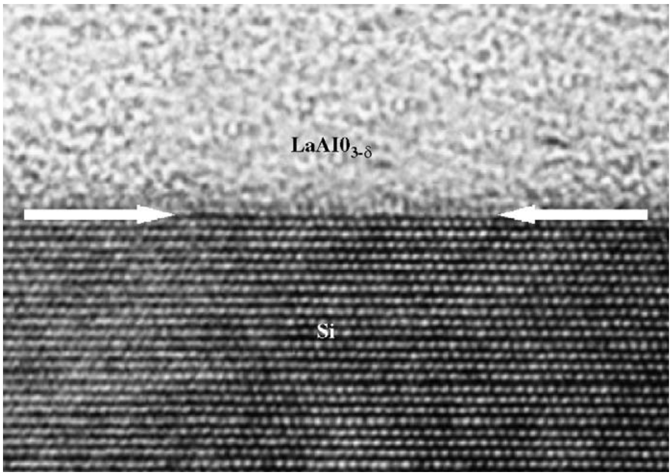

Fig. 1. The cross-sectional HRTEM of the $LaAlO_{2.73}$/Si interface.

$LaAlO_{3-\delta}$ film thickness was 12 nm. The measurements of in situ reflection high-energy electron diffraction (RHEED) and ex situ X-ray diffraction (XRD) show that the $LaAlO_{3-\delta}$ film was amorphous. Fig. 1 gives the cross-sectional high-resolution transmission electron microscope (HRTEM) image of $LaAlO_{3-\delta}$/Si interface. The HRTEM image shows a sharp interface and no inter-penetration or SiO_2. The stoichiometry ratio of La, Al, and O in the $LaAlO_{3-\delta}$ film approached 1:1:2.73 as measured by Rutherford backscattering spectrometry. The electron concentration of the $LaAlO_{2.73}$ film is $3.6\times10^{22}\,cm^{-3}$, and the hole concentration of the p-type Si substrate is $1.4\times10^{15}\,cm^{-3}$ determined by Hall effect measurement, respectively.

In order to determine the characteristics of $LaAlO_{2.73}$/Si heterojunctions, two indium electrodes were attached on the surfaces of $LaAlO_{2.73}$ film and Si substrate (the sample size being $3\times5\,mm^2$) as shown in the insets of Figs. 2 and 4. All measurements were carried out at room temperature.

3. Results and discussion

The *I–V* characteristics of the $LaAlO_{2.73}$/Si p–n heterojunction was measured with a pulse-modulated current source. Good rectifying property was observed. Fig. 2 shows an *I–V* curve of the $LaAlO_{2.73}$/Si p–n heterojunction. The turn on voltage under forward bias and the break down voltage under reverse bias are about 1 and −13.5 V, respectively. The ratio of forward current and reverse current approaches 360 in the applied voltage region from −1.5 to 1.5 V.

The most interesting property of $LaAlO_{2.73}$/Si p–n heterojunction is the ferroelectricity. The polarization versus bias (*P–V*) curve was measured with the RT6000S ferroelectric test system in virtual-ground mode. Fig. 3 shows the *P–V* hysteresis of the p–n heterojunction, in which an increased reverse field was applied at the beginning of the measurement. The hysteresis loop is not closed due to the asymmetric space charges on the two sides of the interface. The remnant polarization (P_r) and coercive field (E_c) for the heterojunction are $2.66\,\mu C/cm^2$ and 3.4 V, respectively. In the heterostructure of n-type $LaAlO_{2.73}$ and p-doped Si, a polarization of space charges is formed perpendicular to the interface due to the electrons in Si diffused from $LaAlO_{2.73}$ and the holes left in $LaAlO_{2.73}$ around the space-charge region. When we start the measurement with an increased reverse bias ($V_{bias}<0$), the built-in field of the system is enhanced, as well as the magnitude of the polarization. When the forward bias ($V_{bias}>0$) is applied, the built-in field will be decreased and thus the polarization is reduced. So we think that the *P–V* loop mainly results from the space charges in the depletion layer of the p–n heterojunction. No ferroelectric loop was observed in the conductive $LaAlO_{2.73}$ film, also giving a support for the enhanced ferroelectricity

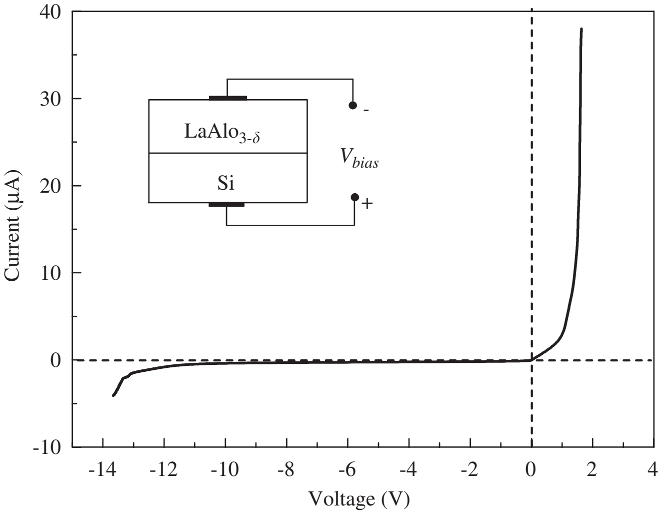

Fig. 2. *I–V* curve of the $LaAlO_{2.73}$/Si p–n heterojunction at room temperature. The inset is the schematic circuit of the sample measurement.

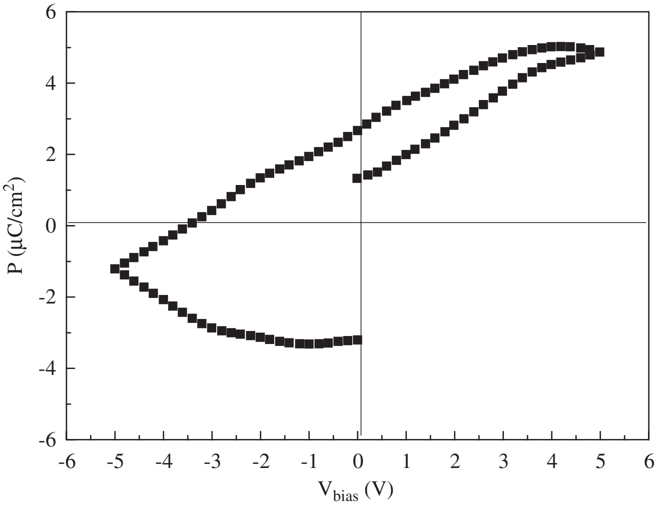

Fig. 3. Ferroelectric hysteresis loop of the $LaAlO_{2.73}$/Si p–n heterojunction.

originating from the interface of the heterojunction. The detailed investigation on the mechanism is underway.

The photovoltaic characteristics were investigated using a 308 nm excimer laser (pulse width ~25 ns) and measured by a 500 MHz oscilloscope (Tektronix TDS3052B). As shown in the inset of Fig. 4, the In electrode was placed at a corner of the $LaAlO_{2.73}$ film surface. The irradiated area was $6\,mm^2$ and the energy density was $60\,mJ/cm^2$. An open-circuit photovoltage at the p–n heterojunction was observed between the two electrodes when the $LaAlO_{2.73}$ surface was irradiated by a 308 nm laser pulse. Fig. 4 shows the typical open-circuit photovoltage V_{oc} as a function of time. The rise time is ~12 ns and the full-width at half-maximum (FWHM) is ~25 ns. The waveform is very symmetrical and the FWHM is in agreement with that of the laser pulse. The experimental result shows that the photovoltaic effect is a fast process. The photovoltaic pulse amplitude V_{oc} increases nearly linearly with laser energy, as shown in Fig. 5.

In order to compare with $LaAlO_{2.73}$/Si p–n heterojunction, the $LaAlO_{2.73}$ film (12 nm thick) was also deposited on the n-type Si substrate to form a $LaAlO_{2.73}$/Si n–n heterojunction under the same growth condition as the $LaAlO_{2.73}$/Si p–n heterojunction. The photovoltaic amplitude of the $LaAlO_{2.73}$/Si n–n heterojunction decreases 3 times compared with that of the p–n heterojunction, since the built-in electric field in the $LaAlO_{2.73}$/Si n–n heterojunction is smaller than that in p–n heterojunction.

According to the semiconductor theory,

$$d = -x_{\mathrm{P}} + x_{\mathrm{N}} = \left(\frac{2\varepsilon_1\varepsilon_2(V_{\mathrm{D}} - V)}{e}\,\frac{N_{\mathrm{A}} + N_{\mathrm{D}}}{N_{\mathrm{A}}N_{\mathrm{D}}}\right)^{1/2}$$

$$= \left(\frac{2\varepsilon_1\varepsilon_2}{eN_{\mathrm{A}}}(V_{\mathrm{D}} - V)\right)^{1/2} (N_{\mathrm{D}} \gg N_{\mathrm{A}}),$$

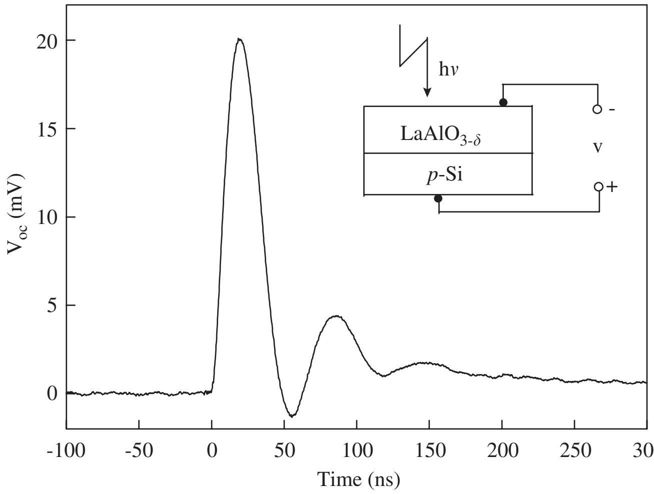

Fig. 4. Transient open-circuit photovoltage varying with time under 308 nm pulsed laser irradiation. Inset displays the schematic circuit of the sample measurement.

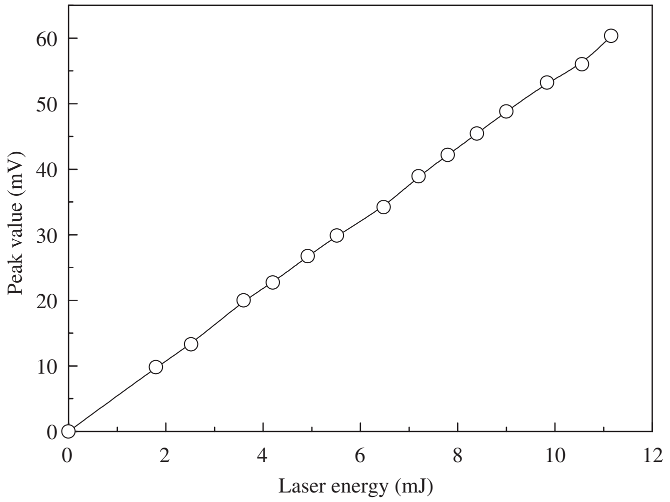

Fig. 5. Peak amplitude of the photovoltage as a function of laser energy under 308 nm pulsed laser irradiation.

where x_{P} and x_{N} are the thickness of the depletion layer of Si and $LaAlO_{2.73}$, respectively; N_{A}, N_{D} are acceptor (Si) concentration and donor ($LaAlO_{2.73}$) concentration; and ε_1, ε_2 are the dielectric constants of Si and $LaAlO_{2.73}$, respectively; V_{D} is the diffusion voltage. When $N_{\mathrm{D}} \gg N_{\mathrm{A}}$, the thickness of the depletion layer is determined by the low concentration, mainly coming from Si side. The photovoltage induced by the 308 nm laser pulse can be explained as the following. The photon energy (~4 eV) of 308 nm laser is greater than the band gap energy of Si (~1.1 eV) but less than that of the amorphous $LaAlO_3$ (~6 eV), suggesting that the 308 nm photons will not excite the nonequilibrium carriers in the $LaAlO_{2.73}$ thin film. But $LaAlO_{2.73}$ with thickness of 12 nm allows the 308 nm laser to pass through the film into the Si substrate, as seen from the absorption spectra of $LaAlO_3$ [8,9]. With the pulsed laser irradiation, excessive electron–hole pairs are generated in the Si substrate. Due to the built-in electric field near the interface of the p–n heterojunction, electrons in the conduction band of Si will drift into $LaAlO_{2.73}$, causing the prompt occurrence of the photovoltage in the system. Although $LaAlO_{2.73}$ is the amorphous state, the fast photoresponse of the junction can be obtained because of the ultrafast photoresponse in Si which is widely used as photodetector.

4. Conclusions

Good I–V rectifying property, ferroelectricity of interface enhancement and fast photovoltaic effect have been observed in the amorphous $LaAlO_{3-\delta}$ and Si p–n heterojunction. The results indicate that the heterojunctions consisting of n-type amorphous and oxygen-deficient provskite oxide with p-type Si also possess better multifunctional properties of rectification, ferroelectricity and photovoltaic effect. We expect that the investigation should open up new possibilities in device development and other applications with the heterojunction of amorphous provskite oxide and Si.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 10334070) and the National Key Basic Research and Development Program of China (Grant No. 2004CB619004).

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