RESISTIVITY CHANGE IN $SrTiO_3$ UPON IRRADIATION AND ITS APPLICATION IN LIGHT SENSING

Sanit Suwanwong[1], Jirapat Kullapapinyokul[1], Tanachat Eknapakul[1], Pornpana Buaphet[1], Rungrueang Pattanakul[2], and Worawat Meevasana[1,3,*]

Received date: February 11, 2014 Revised date: April 11, 2014 Accepted date: April 17, 2014

Abstract

Commercial light sensing devices are usually made of semiconducting materials which have small band gaps (e.g. CdSe, CdS) and hence they are opaque under visible light. In this study, the focused material is transparent strontium titanate ($SrTiO_3$) which has a larger band gap (around 3.2-3.3 eV). The resistivity changes under various types of irradiation at ambient pressure were investigated, by using a sputtering technique for making gold electrodes on $SrTiO_3$ samples. It was found that the resistance of insulating $SrTiO_3$ single crystals could decrease dramatically upon exposure to violet-to-ultraviolet (UV) light sources which were the deuterium lamp and UV light emitting diode (LED) used in our case. The response time of the resistivity change was also investigated. The results suggest that $SrTiO_3$ has the potential usage as a transparent sensor which is responsive in the violet-to-ultraviolet range.

Keywords: Strontium titanate ($SrTiO_3$), light sensing, irradiation effect, oxygen vacancy

Introduction

Today's electronic devices rely largely on the semiconducting properties of materials. While the progress of new developments using conventional semiconductors (e.g. silicon) has nearly reached its limit, new materials (e.g. graphene) have been studied to overcome the problem (Geim and Novoselov, 2007). Besides graphene, two-dimensional electron gases (2DEG) at oxide interfaces (Takagi and Hwang, 2010; Mannhart and Schlom, 2010) also show much potential for electronic devices with functionalities beyond that which conventional semiconductors can offer. The seminally-discovered 2DEGs at the interfaces between $SrTiO_3$ and $LaAlO_3$ show a number of appealing properties, including a high electron mobility (Ohtomo and Hwang, 2004), superconductivity (Reyren *et al*., 2007), and large magnetoresistance (Brinkman *et al*., 2007).

[1] *School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand. E-mail: worawat@g.sut.ac.th*

[2] *Synchrotron Light Research Institute, Nakhon Ratchasima, 30000, Thailand.*

[3] *NANOTEC-SUT Center of Excellence on Advanced Functional Nanomaterials, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.*

[*] *Corresponding author*

Indeed, metal-insulator switching devices in nanoscale have already been demonstrated (Cen *et al*., 2008). From our previous studies, we also found that the charge densities of 2DEGs at oxide surfaces, e.g. $SrTiO_3$ (Meevasana *et al*., 2011) and $KTaO_3$ (King *et al*., 2012), can respond to external stimuli, like irradiations. We also showed that the dielectric constant of $CaCu_3Ti_4O1_2$ could be enhanced upon excitation of the violet laser (Masingboon *et al*., 2013), suggesting some application in novel oxide optoelectronics.

In this article, the focused material is perovskite oxide $SrTiO_3$. Since most of the common light sensors use small-band-gap semiconductors, e.g. CdS and CdSe with band gaps of 2.42 and 1.73 eV, respectively (Mohanchandra and Uchil, 1998; Antohe *et al*., 2003), they are opaque. On the other hand, since $SrTiO_3$ (its atomic structure is shown in Figure 1(a)) has a wider band gap of ~3.3 eV (Benthem *et al*., 2001), it is transparent (see Figure 1(b)) making it possible to be used as a component in transparent electronics. Importantly, the wide-band-gap $SrTiO_3$ could respond better to UV light compared to conventional semiconductors and hence this could be useful in civil and military applications with the need for ultraviolet detectors (Xing *et al*., 2007). While the $SrTiO_3$-based UV detector has been shown possible, here we have investigated further the response to various types of available light sources, including sunlight. The response time periods of on-off switching are measured and discussed; furthermore, we also show that this response time can be modified by externally modifying the circuit.

Materials and Methods

Sample Preparation and Resistance Measurement

The $SrTiO_3$ samples measured in the work (Crystal Base Co., Japan were single crystals with (100) crystal orientation and 5×5×0.5 mm^3

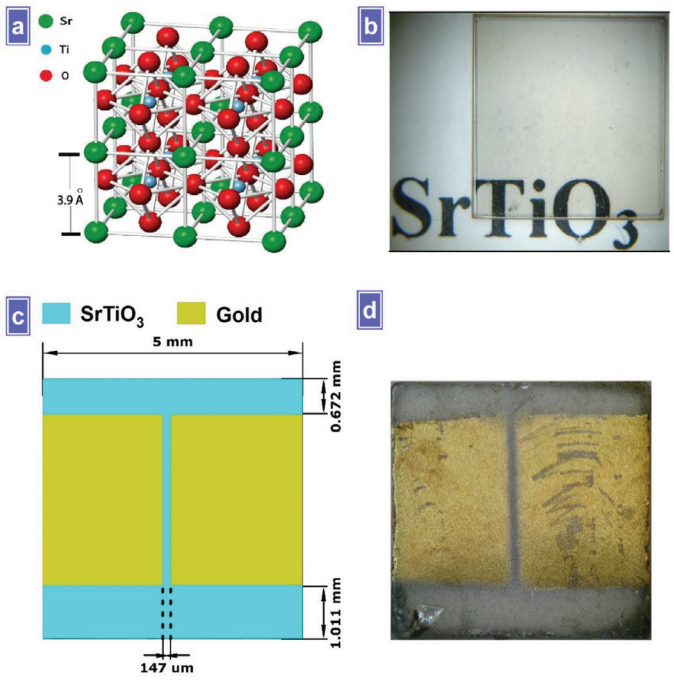

Figure 1. $SrTiO_3$ single crystal. (a) atomic structure of $SrTiO_3$ sample (b) Transparency of $SrTiO_3$ single crystal (c-d) pattern of gold electrodes on the sample surface with using DC sputtering coater

in dimension. The samples were first cleaned with KI/I_2 (KI: I_2: H_2O = 10 g: 2.5 g: 100 ml), and then rinsed with water, acetone, and ethanol. Then gold electrode patterns were created on the samples' surfaces by using a DC sputtering coater. As shown in Figure 1(c)-1(d), the $SrTiO_3$ each surface was covered with gold films except in the middle part whose width was around 147 μm. Note that this width was small to keep the resistance low enough for our measurement but large enough to avoid an electrical shortage.

This middle area of the $SrTiO_3$ surface, which was initially insulating without any excitation, would later be exposed to various types of irradiation, including a violet laser (405 nm), green laser (530 nm), red laser (650 nm), ultraviolet light emitting diode (LED), deuterium lamp (Ocean Optics DH-2000, Ocean Optics Inc., Dunedin, FL, USA), halogen lamp (Ocean Optics DH-2000), and sunlight. To observe the change at the $SrTiO_3$ surface after being irradiated, the surface resistance was measured by an Agilent source meter (model: B2901A, Agilent Technologies, Santa Clara, CA, USA). The setup diagram was shown in the inset of Figure 2(a) and Figure 2(d). For sunlight, the change under both normal and focusing conditions was also measured. A magnifying glass with 14 cm in diameter was used to focus the sunlight; the size of the partially focused spot was around 0.8 cm in diameter.

Results and Discussion

As shown in Figure 2(a), we observed a pronounced change in surface resistance when the sample was exposed to the violet laser with the intensity around 710 W/m^2. The original surface resistance was around 20 GΩ and then decreased quickly to around 200 MΩ after the violet laser was turned on. After the violet laser was turned off, the resistance increased back close to the original value but at a noticeably slower rate. The zoom-in periods during turning on and off the laser were shown in Figure 2(b) and 2(c). By defining the response time to be

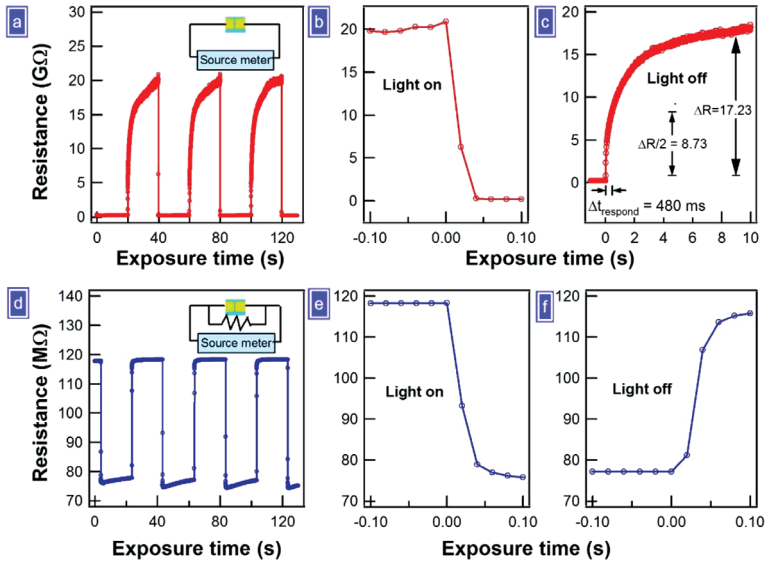

Figure 2. (a) The resistance before and after the violet laser exposure on $SrTiO_3$. The inset shows measurement setup in series. (b-c) The corresponding zoom-in periods when the violet laser is on and off. (d) The resistance before and after the violet laser exposure on $SrTiO_3$ with 180 MΩ resistor added in parallel (see inset). (e-f) The corresponding zoom-in periods when the violet laser is on and off

the period in which resistance changes half way to the saturate value, the response times after turning on and off were extracted to be around 11.9 ms and 480 ms, respectively.

This resistance drop, when the light was on, could be caused by several effects, including the photoconductivity effect (Jiang and Hasegawa, 1999), the photoelectric effect (Sorokin *et al*., 2007), and the creation of oxygen vacancies at the surface (Meevasana *et al*., 2011; King *et al*., 2012). For the photoconductivity and photoelectric effects, the resistance should recover quickly after turning off the light. However, for the oxygen vacancy effect, it could last much longer after turning off the light; the recovery rate could last a very long time, in order of hours, especially under vacuum condition (Meevasana *et al*., 2011). In our case at ambient pressure, the recovery still took relatively long in the order of 480 ms (Figure 2(c)), even in the ambient atmosphere where oxygen was abundant for the recovery to occur. This suggests that the oxygen vacancy effect has the major role in this change; however, we should note that we believe that the photoconductivity and photoelectric effects could still affect the change but to a lesser degree.

Technically, an application which needs the response times between on and off to be in the same order could suffer from this much difference which we observe here (e.g. 11.9 ms versus 480 ms in Figure 2(b) and 2(c)). Therefore, we investigated further and found that, indeed, this difference could be adjusted by external tuning. As shown in Figure 2(d)-2(f), after we connected a 118 MΩ resistor in parallel to the $SrTiO_3$ sample (see inset of Figure 2(d)), the response times, when turning on and off, changed to 14.4 ms and 24.8 ms in Figure 2(e) and 2(f), respectively. However, there was a trade-off effect; although the response time for turning off was reduced significantly, the effective changes in resistance were also much reduced and the turning-on response time also increased slightly.

Besides the irradiation from the violet laser, we also irradiated the $SrTiO_3$ samples by using other various light sources, including red laser, green laser, UV LED, deuterium lamp, halogen lamp, and sunlight. The intensity spectra of these light sources as a function of wavelength by spectrometer (Model: Ocean Optics HR4000) are shown in Figure 3(a). The responses in resistance after turning on and off the light sources are shown in Figure 3(b); note that each change in resistance along the y-axis (in log scale) was normalized by the overall intensity of each light source. The changes in resistance per overall intensity are high when using the deuterium lamp and UV LED. This

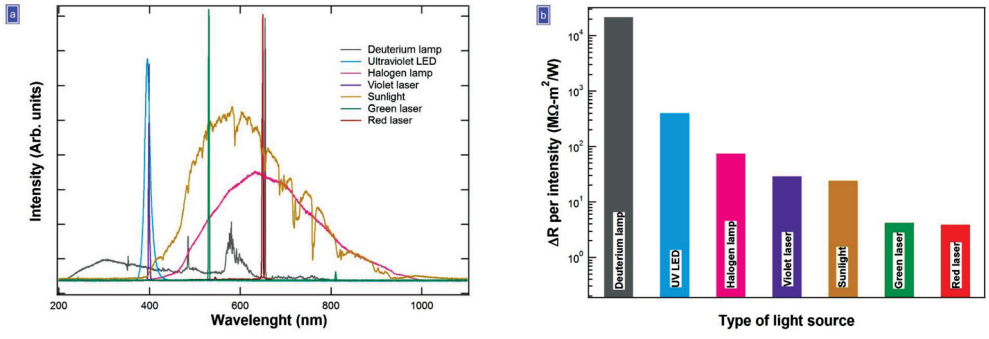

Figure 3. (a) The intensity spectra of various light sources, including the deuterium lamp, UV LED, halogen lamp, violet laser, sunlight, green laser, and red laser as a function of wavelength (the overall intensity for each light source is adjusted to fit in the graph). (b) The responses in resistance after turning on and off the light sources; note that each change in resistance is normalized by the overall intensity of each light source

suggests that the resistance change of $SrTiO_3$ is more sensitive in the UV range. The deuterium lamp has a large spectral weight of a wavelength below 387 nm, i.e. a photon energy higher than the band gap of 3.2 eV. Note that the halogen lamp also has some spectral weight of a wavelength below 387 nm but may be hard to visualize in Figure 3(a); this part of the spectrum could be the main contribution to the change of resistance shown in Figure 3(b) for the halogen lamp. For the violet laser, the wavelength is around 405 nm or 3.06 eV (just below the band gap); it can be seen that the change per intensity is relatively much lower compared to the 2 light sources above; this corresponds quite well with the onset of the spectral response of $SrTiO_3$ (Xing *et al*., 2007). For the red and green lasers, the changes are much lower, at least 3 orders of magnitude lower compared to the UV LED, but still finite. While these finite changes should be checked further, possible reasons may be due to two-photon excitation (Catalano *et al*., 1974) or local heating.

We also investigated further to see the resistance change under the different intensity of sunlight, as shown in Figure 4. In the measurement, we used a magnifying glass to focus the sunlight and hence increased the intensity to around 4400 W/m^2 while the unfocused intensity was 916 W/m^2. It was observed that the resistance change (Figure 4) could largely depend on the intensity. When there was no light, the resistance was around 23 GΩ, and the resistance dropped to 6.2 GΩ under indoor light, to 505 MΩ under unfocused light, and 10 MΩ under focused light. This pronounced change and its variations suggest that the $SrTiO_3$ detector can also be used for detecting the intensity of sunlight at a quantitative level. The mapping of the resistance change versus intensity variation will be investigated further. While the samples here are single crystals, in the future we are also interested in other titanium oxides prepared by various methods, e.g. WO_3 film (Paipitak *et al*., 2012) and $BaTiO_3$ film (Hodak *et al*., 2010).

Conclusions

In this article, we show that the surface resistance of transparent $SrTiO_3$ material could be reduced largely under irradiation from various light sources, especially the deuterium lamp and UV LED. The intrinsic response times, when the light is on and off, can be different by around 1 order of magnitude but this difference can be adjusted externally. We also show that the resistance change can also largely depend on the sunlight intensity. These results show the promise of the light-sensing application of this transparent $SrTiO_3$ material.

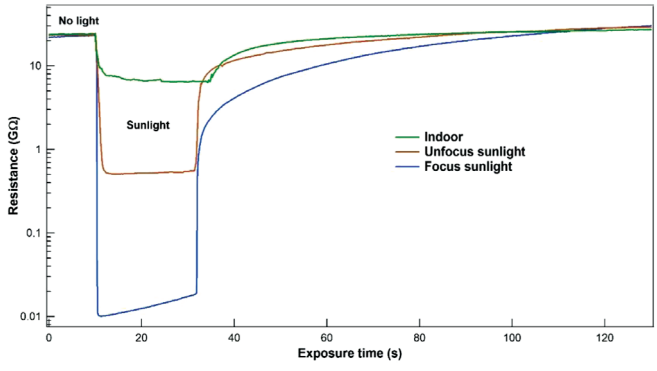

Figure 4. The resistance before and after sunlight exposure on $SrTiO_3$, using indoor, unfocused sunlight, and focused sunlight

Acknowledgements

This work was supported by the Suranaree University of Technology (OROG) and the Office of Higher Education Commission's National Research Universities.

References

Antohe, S., Ion, L., and Antohe, V. A. (2003). The effect of the electron irradiation on the structural and electrical properties of AII-BVI thin polycrystalline films. J. Optoelectron. Adv. M., 5(4):801-816.

Benthem, K.V., Elsasser, C., and French, R.H. (2001). Bulk electronic structure of $SrTiO_3$: Experiment and theory. J. Appl. Phys., 90(12):6156-6164.

Brinkman, A., Huijben, M., Van Zalk, M., Huijben, J., Zeitler, U., Maan, J.C., Van Der Wiel, W.G., Rijnders, G., Blank, D.H.A., and Hilgenkamp, H. (2007). Magnetic effects at the interface between non-magnetic oxides. Nat. Mater., 6:493-496.

Catalano, I.M., Cingolani, A., and Minafra, A. (1974) Transmittance, luminescence, and photocurrent in CdS under two-photon excitation. Phys. Rev. B, 9:707.

Cen, C., Thiel, S., Hammerl, G., Schneider, C.W., Andersen, K.E., Hellberg, C.S., Mannhart, J., and Levy, J. (2008). Nanoscale control of an interfacial metal-insulator transition at room temperature. Nat. Mater., 7:298-302.

Geim, A.K. and Novoselov, K.S. (2007). The rise of graphene. Nat. Mater., 6:183-191.

Hodak, S.K., Supasai, T., Wisitsoraat, A., and Hodak, J.H. (2010). Design of low cost gas sensor based on SrTiO3and $BaTiO_3$ films. J. Nanosci. Nanotechno., 10:7236-7238.

Jiang, C. S. and Hasegawa, S. (1999). Photoconductivity of the Si(111)-7 x 7 and x -Ag surfaces. Surf. Sci., 427-428:239-244.

King, P.D.C., He, R.H., Eknapakul, T., Buaphet, P., Mo, S.-K., Kaneko, Y., Harashima, S., Hikita, Y., Bahramy, M.S., Bell, C., Hussain, Z., Tokura, Y., Shen, Z.-X., Hwang, H.Y., Baumberger, F., and Meevasana, W. (2012). Subband structure of a two-dimensional electron gas formed at the polar surface of the strong spin-orbit perovskite $KTaO_3$. Phys. Rev. Lett., 108:117,602.

Mannhart, J. and Schlom, D.G. (2010). Oxide interfaces-An opportunity for electronics. Science, 327(5,973):1607-1611.

Masingboon, C., Eknapakul, T., Suwanwong, S., Buaphet, P., Nakajima, H., Mo, S.-K., Thongbai, P., King, P.D.C., Maensiri, S., and Meevasana, W. (2013). Anomalous change in dielectric constant of $CaCu_3Ti_4O1_2$ under violet-to-ultraviolet irradiation. Appl. Phys. Lett., 102:202,903.

Meevasana, W., King, P.D.C., He, R.H., Mo, S.-K., Hashimoto, M., Tamai, A., Songsiriritthigul, P., Baumberger, F., and Shen, Z.-X. (2011). Creation and control of a two-dimensional electron liquid at the bare $SrTiO_3$ surface. Nat. Mater., 10:114-118.

Mohanchandra, K.P. and Uchil, J. (1998). Electrical properties of CdS and CdSe films deposited on vibrating substrates. J. Appl. Phys., 84(1): 306-310.

Ohtomo, A. and Hwang, H. (2004). A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface. Nature, 427:423-426.

Paipitak, K., Rattanarak, J., Pakdeeyingyong, D., Techitdheera, W., Porntheeraphat, S., and Pecharapa, W. (2012). Enhanced electrochromic performance of sol-gel derived WO_3 thin films assisted by electrospun PVA nanofibers. Adv. Mat. Res., 528:249-253.

Reyren, N., Thiel, S., Caviglia, A.D., Fitting Kourkoutis, L., Hammerl, G., Richter, C., Schneider, C.W., Kopp, T., R etschi, A.-S., Jaccard, D., Gabay, M., Muller, D.A., Triscone, J.-M., and Mannhart, J. (2007). Superconducting interfaces between insulating oxides. Science, 317:1196-1199.

Sorokin, A.A., Bobashev, S.V., Feigl, T., Tiedtke, K., Wabnitz, H., and Ritchter, M. (2007). Photoelectric effect at ultrahigh intensities. Phys. Rev. Lett., 99:213,002.

Takagi, H. and Hwang, H.Y. (2010). An emergent change of phase for electronics. Science, 327(5973):1601-1602.

Xing, J., Zhao, K., Lu, H.B., Wang, X., Liu, G.Z., Jin, K.J., He, M., Wang, C.C., and Yang, G.Z. (2007). Visible-blind, ultraviolet-sensitive photodetector based on SrTiO3 single crystal, Opt. Lett., 32(17):2526-2528.