ON THE ORIGIN OF FERROELECTRIC PHOTOVOLTAIC EFFECTS IN VERTICAL $BiFeO_3$ HETEROSTRUCTURES

AMR AHMED KORANY ABDELSAMIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

Thesis title: On the origin of ferroelectric photovoltaic effects in vertical $BiFeO_3$ heterostructures

Abstract

Developing clean and sustainable energy sources has become increasingly importantto humankind. Specifically, solar energy which is abundant and can be directly converted into electricity that is essential for modern life. *Photovoltaic cells* (PVs) are the constructed platforms to convert sunlight into electrical power. A typical solar cell consists of *p-type/n-type* bilayer made of silicon. In these devices, the emergent electrochemical potential difference at their interface establishes an electric field that assists in separating the photoexcited charges. This implies that the output photovoltage is limited by the material's bandgap. In fact, in terms of efficiencies, Shockley-Queisser (SQ) model anticipated maximum power conversion efficiency of 33.7% in semiconductor of bandgap 1.34 eV. Unfortunately, this theoretical limit is approaching, and alternative solutions are required. On the other hand, *Bulk photovoltaic cells* are potential substitutes to junction solar cells. They rely on noncentrosymmetric crystals, such as *ferroelectrics*, as an active layer. In these cells, the photoexcited charge carriers can be separated throughout the bulk of the crystal. Accordingly, the output photovoltage is not related to the material's bandgap, and hence sky-high open-circuit voltages can be reached. Moreover, the construction of the cell is simpler if compared to the commercial solar cells comprising pn- or pin-junctions or tandem cells.

Despite its discovery in 1956, it was only 2009 when the interest in bulk photovoltaic effects was renewed upon the emergence of switchable PV behavior in *$BiFeO_3$* crystals. Since then, much effort has been dedicated in attempt to explain the mechanism of photovoltaic effects in ferroelectrics since the cell structure is complicated assuming the existence of multiple potential charge separation sources. This resulted in divided opinion on whether Schottky barrier, domain wall, bulk effects or even a combination of these effects are behind such interesting behavior that can be termed *ferroelectric photovoltaic effect*. This motivated this work which employs the prototypical ferroelectric bismuth ferrite ($BiFeO_3$) films sandwiched between two metallic electrodes.

This experimental dissertation aims at the fabrication and characterization of single crystalline $BiFeO_3$-based photovoltaic cells. For this, a physical vapor deposition technique, namely, pulsed laser deposition (PLD), is adopted to fabricate the devices. Bismuth ferrite

films were first probed and analyzed for their crystal and ferroelectric structures. Afterwards, the electrical properties were examined under either white or monochromatic lights revealing the photovoltaic property of the devices under test.

A direct evidence of the predomination of Schottky barrier is revealed in $BiFeO_3$ by illuminating the devices with unpolarized white light. By systemically studying the thickness-dependent photovoltaic behavior in $BiFeO_3$ films ranging from 38 to 500 nm, the thinnest film showed a one order-of-magnitude higher current density. The measured behavior indicates the PV response stemmed from the interface effect. In this context, the thinner the film, the more efficient is the charge carrier collection. Also, the top interface was modulated from Schottky to ohmic characters which further endorsed the obligation of Schottky barrier presence to promote photovoltaic behavior in ferroelectric photovoltaics. Furthermore, oscillating photocurrents are measured in vertical $BiFeO_3$ capacitors under linearly polarized light. When the sample is illuminated by linearly polarized white or 520 nm lights, the photocurrent is maximized [-110], or normal to in-plane polarization. This is found to be consistent with the linear dichroism in $BiFeO_3$ and indicates the domination of interface band-bending PV. On the other hand, shone by linearly polarized 405 nm laser, bulk PV came to picture manifested by the photocurrent spiking along the in-plane polarization which was confirmed by the theoretical calculations of bulk PV.

The findings provide insights into fundamental and technological perspectives of the ferroelectric photovoltaic effects. Fundamentally, it offers new understanding of light-matter interaction in ferroelectrics revealing two competitive phenomena, namely, linear dichroism and bulk photovoltaic effect. Moreover, the outcomes pave the way to enhance the PV output in ferroelectrics for solar cells and optoelectronic applications. Also, it establishes grounds for developing self-powered linearly polarized light photodetectors.