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Effect of UV Laser Irradiation on the properties of NiO films and ZnO/NiO Heterostructures

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ABSTRACT

The present work accentuates the effect of UV laser irradiation on the conductivity of nickel oxide (NiO) thin films, deposited at various temperatures by radio-frequency reactive sputtering of Ni in oxygen containing atmosphere. The effect of UV irradiation on zinc oxide – nickel oxide heterostructures, obtained by sputtering, was examined as well. It was found that the resistivity of NiO changes from 12 Ω-cm to 0.62 Ω-cm, and the majority carrier concentration from 3.95×10^{17} holes/cm^3 to 4.22×10^{20} electrons/cm^3. The current-voltage (I-V) characteristics of the ZnO/NiO heterostructure shows an improved p-n diode behavior with the forward bias current increasing for the laser-irradiated ZnO/NiO compared to the as-deposited stack. The observed improvement in diode-like behavior suggests that laser irradiation can be an important technique to controllably change the structural, electrical and optical properties of metal oxide thin films.

INTRODUCTION

Point defects play an important role in determining the electrical, optical and magnetic properties of metal oxide semiconductors. These defects can be introduced using nonequilibrium electronic, photonic and ion irradiation processes. Recent studies indicate laser irradiation as an effective source for a controlled electronic excitation resulting in an enhancement in material properties [1-3]. Laser irradiation creates oxygen vacancies on the surfaces which diffuse into the bottom layers via an interstitial-substitutional mechanism. Nickel oxide is a wide band gap (~3.4eV), intrinsic p-type semiconductor and finds potential applications in UV LEDs [4], Electrochromic devices [5], and as hole transporting interfacial layer in solar cells [6]. NiO in its bulk form is considered to be a Mott (charge transfer) insulator with a resistivity of 1,000 MΩ-μm [7] and crystallizes in the rock-salt cubic structure. Hence, depositing NiO as thin film results in a semi-conducting nature with high resistivity. Further reduction in the resistivity can be obtained by post-deposition treatment like annealing or laser irradiation. The d-d transitions in the valence and conduction bands lead to a strong absorption in the visible spectrum giving a chemically stable pale green color to the oxide. Conductivity change [7] and homojunction p-n diodes [8] based on laser irradiation on NiO thin films were studied previously and provided future scope for researchers.

Zinc oxide (ZnO) has been even more fascinating for many researchers because of its wide range of applications arising due to its intrinsic n-type characteristic and direct wide bandgap (~3.37eV) such as UV LEDs and rectifying device applications [9]. ZnO crystallizes in the wurtzite structure and is typically resistant to damage by energetic particles because of its highly mobile interstitial pairs allowing for a fast annihilation at room temperatures [10]. Unique properties such as large exciton binding energy, large piezoelectric constants and strong luminescence distinguish ZnO from other transition metal oxide semiconductors [11]. Excimer laser irradiation on ZnO has been reported in [12-14] which showed significant changes in structural, optical and electrical properties.

In this report, we present electrical tunability of NiO thin films by laser irradiation of varying number of pulses with good reproducibility. The effect of nanosecond UV laser irradiation, using the 4th harmonic Nd:YAG laser line with λ=266nm, on the properties of the NiO and ZnO/NiO hetetrostructure was studied. Changes in crystalline orientation and charge carrier type and concentrations are observed without any observable film degradation. Point defects arising from the laser irradiation such as vacancies and interstitials play a major role in altering the electrical and optical properties.

EXPERIMENTAL DETAIL

NiO and ZnO thin films were deposited on a glass substrate using a 3-in diameter Ni metal target (99.99% pure) and a 2-in diameter ZnO ceramic target by reactive and RF sputtering respectively. NiO films were deposited under what we found to be optimal O_2/Ar ratio at RT, 300^{o}C and 400^{o}C. The depositions conditions are listed in Table 1. The NiO and ZnO film thicknesses was measured to be 200 nm using profilometry (Dektak) and verified to be consistent with ellipsometric calculations. Subsequently, Laser irradiation on NiO films were performed in room temperature with laser fluence of 150mJ/cm^2 for different number of pulses. The laser fluence is kept below the threshold of physical damage. The electrical properties were measured using a Hall effect measurement setup at room temperature in a magnetic field of +/-2500 Gauss. The resistivity values, obtained from the Hall effect measurement, were in good agreement with those from four probe measurements. A Keithley parameter analyzer with bias voltages ranging from -2V to 3V was used to measure I-V characteristics of the as-deposited and laser-irradiated NiO/ZnO stack.

Table I. Deposition parameters for NiO thin film.

Target	**3-in diameter Nickel metal (99.99% pure)**
Substrate	Glass
Sputtering pressure	9mTorr
Sputtering gas	Ar:O_2 = 20:80
RF Power	95W
Substrate Temperature	RT, 300^{o}C, 400^{o}C
Target to substrate distance	8cm

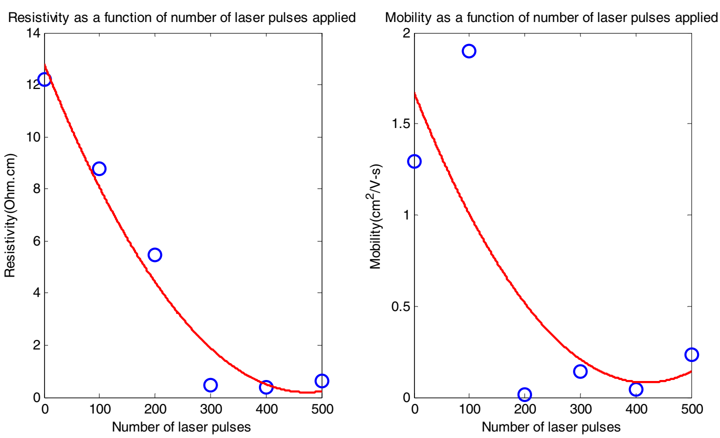
RESULTS AND DISCUSSION

Electrical Changes

Hall effect measurements were performed on as-deposited and laser irradiated NiO samples for different number of pulses in order to determine any change in the electrical properties. It can be observed from Figure 1 that there is a sharp decrease in the resistivity from 12 Ω-cm for as-deposited NiO film to 0.62Ω-cm for 500 pulses of laser fluence 150mJ/cm^2. Laser irradiation likely creates Ni interstitials and O vacancies leading to an increase in the carrier concentration. This can be seen in Figure 2, where the carrier density increases from 3.95×10^{17} holes/cm^3 for as-deposited sample to 3.87×10^{20} holes/cm^3 for up to 400 laser pulses. For irradiation with 500 laser pulses, there is a further increase in the carrier concentration but, more importantly, the conductivity changes to n-type.

At this time, we can only speculate as to the mechanism of these laser-induced conductivity changes and we intend to study this further. It is known that in reactive sputtering deposition of NiO in Ar:O_2 atmosphere, the partial pressure of O_2 determines the rate of generation of Ni vacancies and interstitials. XPS data [15-18] reveal the existence of Ni^{2+}, Ni^{3+} as well as neutral Ni^0 states in such films, which means that the film consists of a mixture of NiO and Ni_2O_3 phases. Upon laser irradiation with up to 400 pulses, a conversion of Ni^{2+} species into Ni^{3+} species may be responsible for the increased hole concentration. Upon applying even higher laser pulse number, up to 500 in our case, a substantial fraction of Ni^0 (interstitials) may be forming, leading to the creation of large free electron concentration[7] that compensates entirely the holes concentration and converts the material into n-type.

As the carrier density increases, the carries become less mobile, as observed from the Hall effect data, most likely due to the disorder induced by the laser irradiation. Table 2 summarizes the electrical properties of as-deposited and laser irradiated NiO films.



(a) (b)

Figure 1. (a) Resistivity **(b)** Mobility w.r.t number of pulses (the curve is just a guide to the eye).

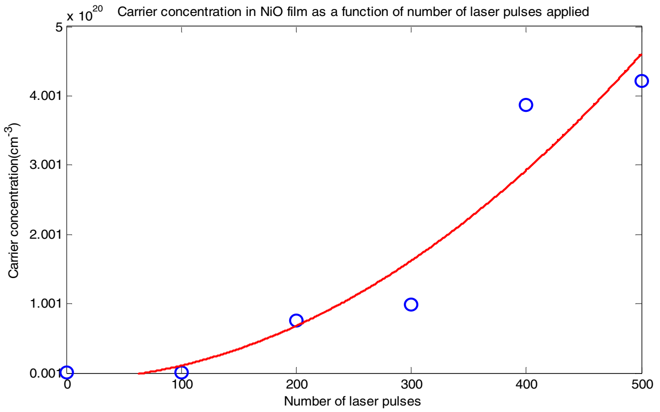


Figure 2. Carrier concentration w.r.t number of laser pulses (the curve is just a guide to the eye).

Table II. Electrical Properties of as-deposited and Laser irradiated NiO films.

200nm NiO	Resistivity(Ω.cm)	Mobility(cm^2/V.s)	Density (/cm^3)	Carrier Type
As-deposited	12.21	1.29	3.95 $x10^{17}$	holes
100 pulses	8.76	1.90	3.75$x10^{17}$	holes
200 pulses	5.48	0.015	7.54$x10^{19}$	holes
300 pulses	0.44	0.142	9.83$x10^{19}$	holes
400 pulses	0.39	0.041	3.87$x10^{20}$	holes
500 pulses	0.62	0.23	4.22$x10^{20}$	electrons

Effect of UV laser irradiation on ZnO/NiO heterostructure

From [19], Al/ZnO proves to be a good ohmic contact along with Ni/NiO interface. Hence, we deposit Al/ZnO/NiO/Ni heterojunction device with Al and Ni metal contacts thickness of 200nm each. I-V characteristics were performed using a keithley semiconductor parameter analyzer on ZnO/NiO (as-deposited) heterostructure and ZnO/NiO (laser irradiated with 400 pulses) to analyze the effect of laser irradiation on ZnO/NiO stack and the voltage is swept from -2V to 3V. It can be observed from Figure 3 that the diode-like characteristics are obtained for both the heterojunctions. For the as-deposited stack, there is a reverse bias current of 8mA for a voltage bias of -2V and a forward bias peak current of 35mA for a voltage bias of 3V. Similarly, for the laser treated stack, there is a there is a reverse bias current of 0.05mA for a voltage bias of -2V and a forward bias peak current of 45mA for a voltage bias of 3V, suggesting an enhanced I-V performance in the forward bias. This enhancement in the diode characteristics is attributed to the change in carrier concentration due to laser irradiation (from Table 2). Since there are more holes in the laser treated ZnO/NiO stack than compared to the as-deposited ZnO/NiO stack, there is a free flow of carriers across the depletion region in forward bias resulting in an enhanced forward bias diode characteristics.

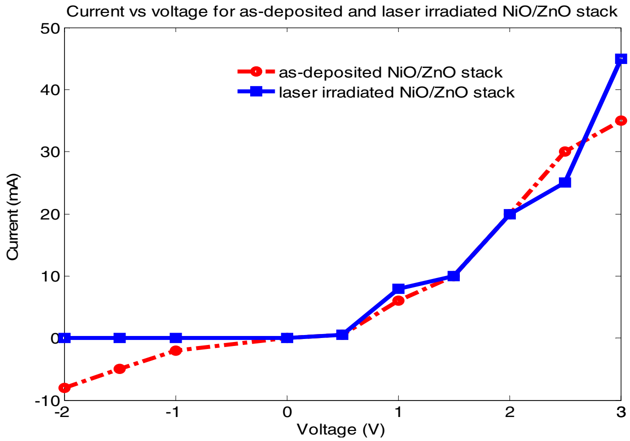


Figure 3. Current-Voltage (I-V) characteristics of as-deposited NiO/ZnO and laser irradiated NiO/ZnO heterostructure.

CONCLUSION

This work has shown that pulsed UV laser irradiation can induces electrical changes in the reactively sputtered NiO thin films in a controllable fashion. Perhaps even more importantly, the conductivity type can be changed from p-type to n-type upon properly choosing the number of pulses applied. The current-voltage (I-V) measurements show significant change in the forward bias current, which is likely due to formation of oxygen defects and nickel vacancies resulting in an increase in carrier concentration in the laser irradiated NiO films. The results obtained for the p-n heterojunction are encouraging to pursue further research on laser irradiation assisted fabrication for light emitting and other applications.

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