Reversible electronic phase transition and Debye temperature of $NiFe_2O_4$ thin film surface

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Abstract

In X-ray photoelectron spectroscopy (XPS) of $NiFe_2O_4$ thin film, the Ni and Fe $2p_{3/2}$ core level binding energies show strong indications that a reversible transition between a more dielectric and a more metallic phases of $NiFe_2O_4$ film is possible. The XPS of Ni and Fe $2p_{3/2}$ core levels for the $NiFe_2O_4$ thin film at room temperature showed large photovoltaic surface charging leading to core level binding energy shifts, characteristic of a highly dielectric (or insulating) surface of $NiFe_2O_4$ thin film at room temperature. This photovoltaic surface charging, seen in the XPS binding energies of the Ni and Fe $2p_{3/2}$ core levels, decreased with increasing temperature, indicating that the $NiFe_2O_4$ thin film became more metallic at elevated temperatures. The photovoltaic surface charging was absent at 538 K indicating metallic nature of the thin film. When the thin film was cooled down to room temperature, the core level binding energy shifts, due to photovoltaic surface charging, were observed again. This indicates that there exists a reversible non-metal to metal phase transition of the $NiFe_2O_4$ thin film with temperature. This work illustrates a route to regulate the surface metal-to-insulator transition in $NiFe_2O_4$ thin film. Furthermore, effective surface Debye temperature has been estimated for the $NiFe_2O_4$ thin film.

Motivation

Inverse spinel ferrimagnetic materials like $NiFe_2O_4$, $CoFe_2O_4$, $NiCo_2O_4$, etc., are often given attention in the context of magnetic properties and/or spintronics.

However, is it possible that such materials have potential for future beyond CMOS devices using electronic properties? Do these materials have some novel features that can be exploited for the device applications? We want to answer these questions.

XPS of metallic and dielectric (non-metallic) samples

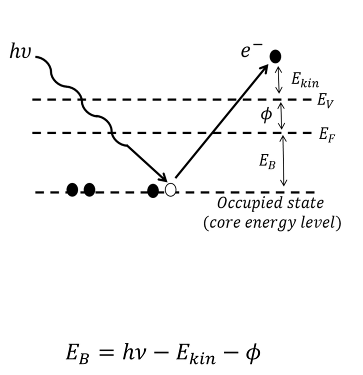

Fig. 1. A simple representation of X-ray photoemission & equation obeying energy conservation during the process.

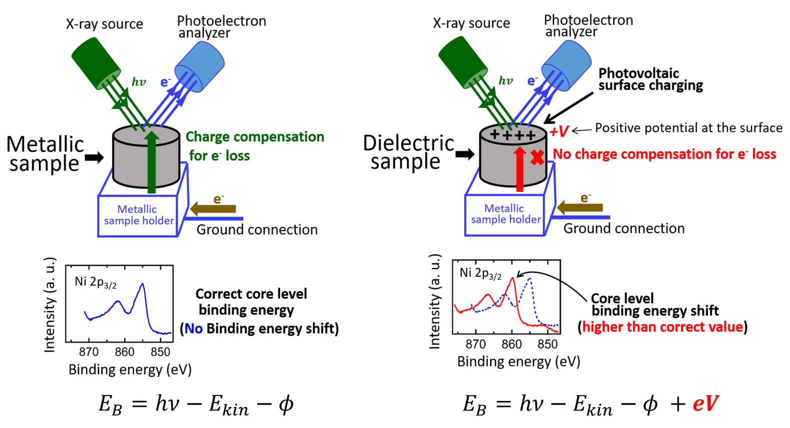

Fig. 2. The XPS of a metallic sample (left) leading to the correct core level binding energy of an element. XPS of dielectric sample (right) results in core level binding energy shift due to positive potential developed at the surface (also known as **surface charging**), due to electron loss from the surface in photoemission. **For a non-metallic phase (metallic phase) of a specimen, there is surface charging (no surface charging) in XPS measurements.**

Temperature dependent XPS of $NiFe_2O_4$ thin film

1. Partially reversible non-metal to metal phase transition

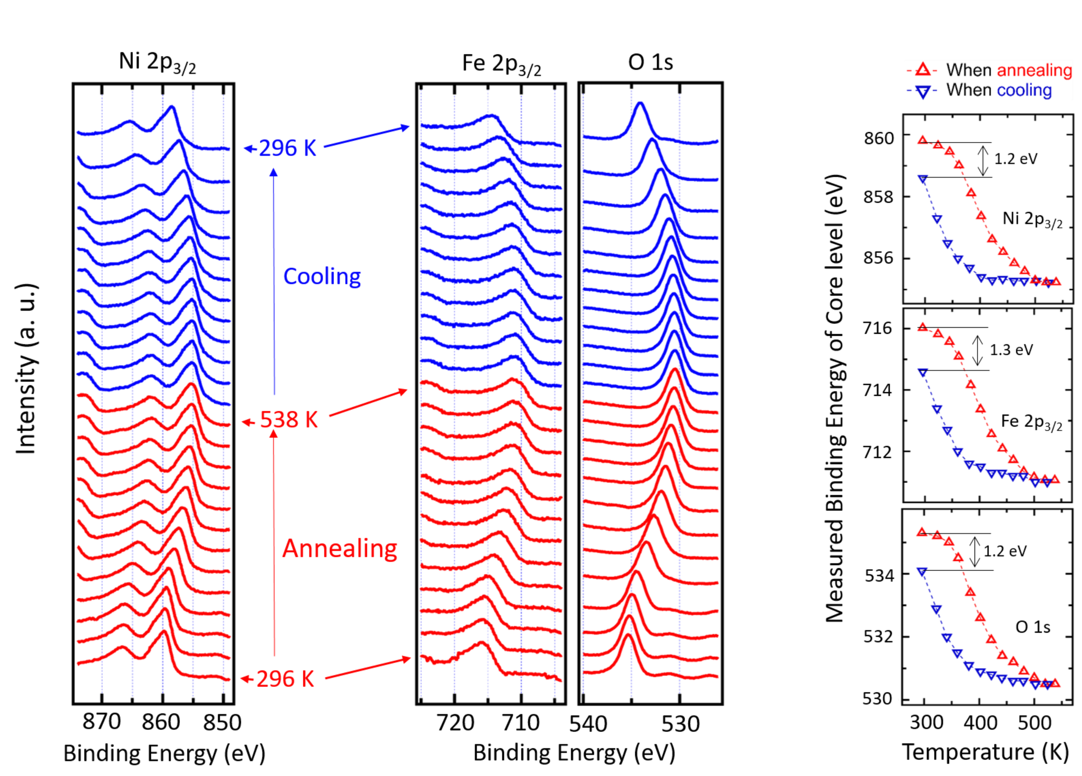

Fig. 3. The XPS spectra of core levels of Ni, Fe, and oxygen at different temperatures.

- Main peak positions of the XPS spectra (Fig. 3) represent binding energies of the core levels of the elements.

<u>**Annealing of the sample from room temperature (296 K) to 538 K**</u>

- At the beginning of the annealing cycle at 296 K, all core level binding energies have highest values (high binding energy shifts), meaning that sample was in **non-metallic phase.**
- The higher the temperature, the lower the core level binding energies, meaning that the sample became more metallic at the higher temperatures.
- At (or near) 538 K, the core level binding energies were correct [1] suggesting no measurable surface charging. For example, the binding energy for Ni $2p_{3/2}$ at 538 K was 855.3 eV, which is in excellent agreement with correct value of 855.4 eV [1].
- **The thin film surface hence became metallic at (or near) 538 K.**
- There is an electronic phase transition of the $NiFe_2O_4$ thin film surface from non-metallic phase to metallic phase when annealed.

<u>**Cooling of the sample from 538 K to room temperature**</u>

- Cooling the sample slowly increased the binding energies: sample slowly became dielectric (non-metallic) again, with decreasing temperature.
- However, perfect restoration of original core level binding energies was not observed: binding energy values at room temperature after the cooling cycle have offset of 1.2±1 eV (Fig. 3).

What's going on? Is it possible to achieve perfect reversibility between the phases?

- The surface might have lost oxygen at higher temperatures.

2. Perfect reversible non-metal to metal phase transition

- After previous temperature dependent XPS, the thin film was annealed in sufficient oxygen and previous dielectric nature was restored.
- XPS was carried out in order to check the possibility of the perfect reversibility.

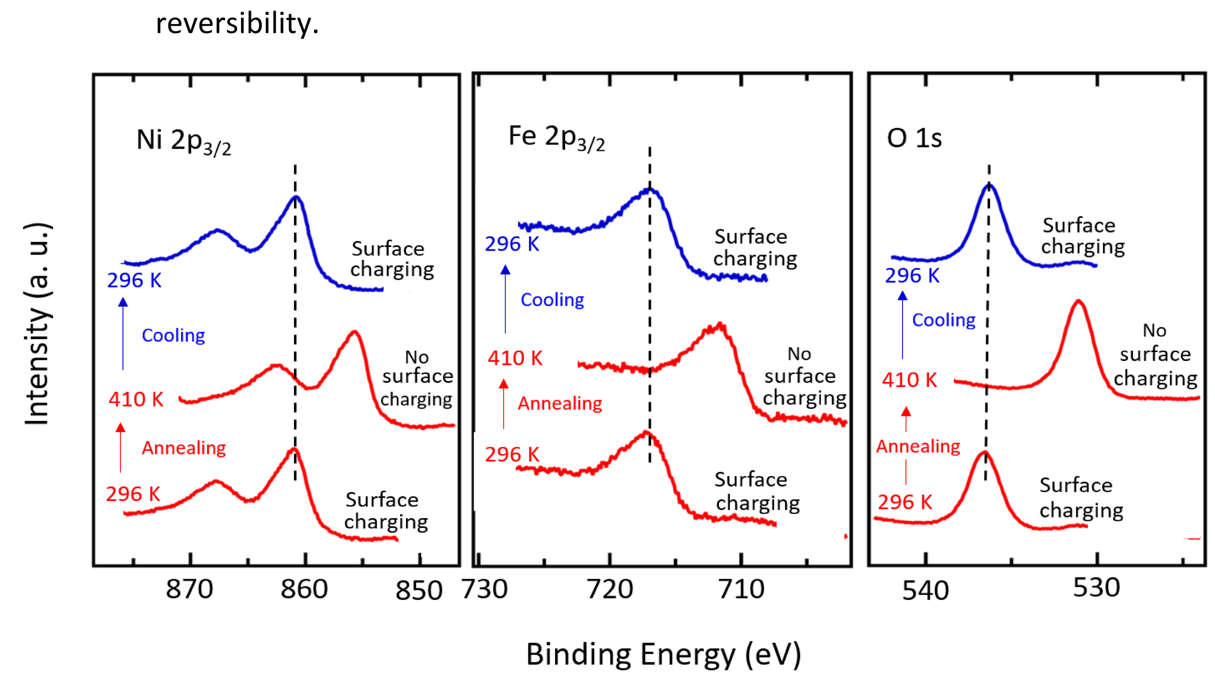

Fig. 4. XPS at 296 K (just before annealing), at 410 K (annealing), and at 296 K (after cooling from 410 K).

- In order to avoid creation of more oxygen defects at the surface, only one higher temperature (410 K) XPS was carried out (Fig. 4).
- Perfect reversibility between non-metallic phase (surface charging in XPS) and metallic phase (no surface charging in XPS) can be achieved, as indicated by dashed vertical lines (Fig. 4).

Any future potential applications of such reversible phase transition property?

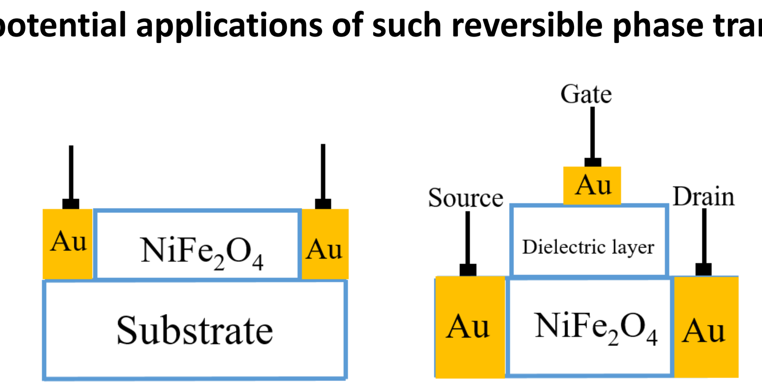

Fig. 5. A simple schematic of two (left) and three (right) terminal device architectures for the material (example $NiFe_2O_4$ thin films) undergoing reversible metal to insulator phase transition [2]. The high-resistance insulating state and the low-resistance metallic state can be switched and hence the property is useful in switching devices [2].

References

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Surface Debye temperature using low energy electron diffraction (LEED)

- The intensities of LEED can be used to get effective surface Debye temperature (θ_D), using Debye-Waller factor [3, 4]:
  $I = I_0 e^{-2W(T)}$,
  $W(T) = \frac{3(\hbar \triangle k)^2 T}{2mk_B\theta_D{}^2}$, where the notations have usual meaning and m is mass of the scatterer.

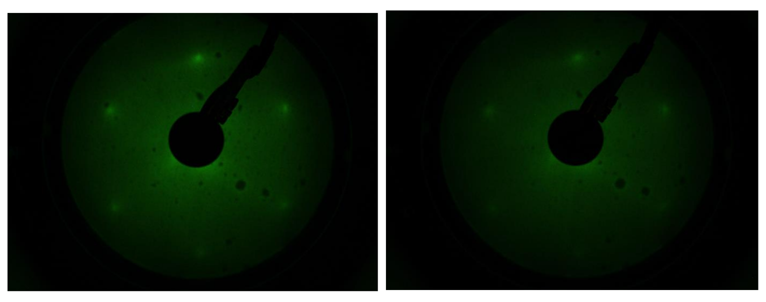

Fig. 6. LEED of $NiFe_2O_4(111)$ thin film taken at 133 eV electron energy at 296 K (left) and 384 K (right).

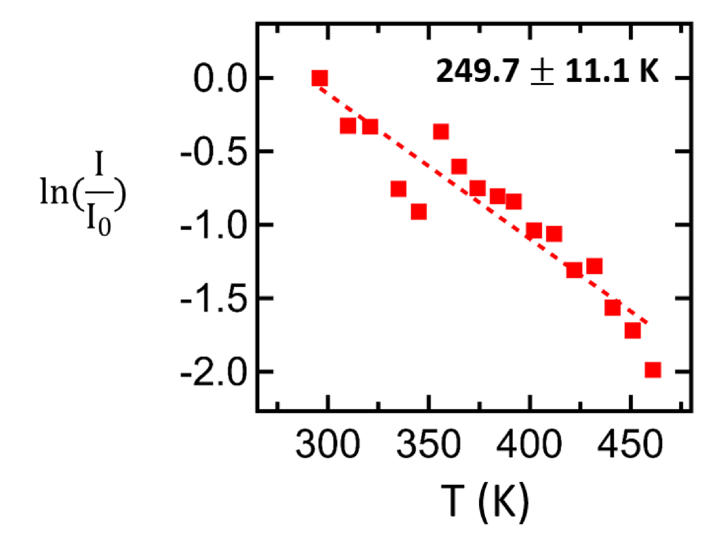

Fig. 7. The effective surface Debye temperature from temperature dependent LEED.

- Higher surface Debye temperature physically indicates harder surface.
- With the surface Debye temperature of 249.7±11.1 K, the surface of $NiFe_2O_4$ thin film is softer than Cr_2O_3, which has surface Debye temperature of around 490 K [3], but harder than the surface of $La_{0.65}Pb_{0.35}MnO$ whose surface Debye temperature could be as low as about 77 K [4].

Conclusions and outlook

- The $NiFe_2O_4$ thin film surface can undergo perfect reversible non-metal to metal phase transition with temperature, opening the doors for future beyond CMOS devices.
- The surface oxygen defects may prevent the phase transition of the $NiFe_2O_4$ thin film surface from being perfectly reversible.
- Temperature dependent LEED intensity showed that the effective surface Debye temperature of $NiFe_2O_4$ thin film is 249.7±11.1 K.
- For the better fundamental insights, temperature dependent X-ray absorption measurement, could be carried out using polarized light, which could give us both electronic and magnetic properties across the phase transition.
- A study to carry out could be whether the thickness of the film affects the nature of the phase transition.
- Since the film is highly crystalline, experimental electronic band structure investigation can be and should be carried out to microscopically understand the surface properties.
- The proportion of Ni to Fe in $NiFe_2O_4$ thin film could be changed (or some other preparation conditions could be changed) during the sample preparation to see how that can affect the phase transitions and other properties to eventually make the material more attractive for device applications.

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