

Hole Doping Through Indium Intercalation Into Nickel Phthalocyanine

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Abstract. A new intercalation of indium and nickel phthalocyanine (NiPc) thin films is developed by using thermal co-evaporation technique. X-ray diffractometer (XRD) and optical absorption spectroscopy of In-doped NiPc suggest the crystal structure of In-doped NiPc is α -phase as same as that of pristine NiPc. Current-voltage characteristic of Schottky diode fabricated with In-doped NiPc thin film shows the enhancement of charge carrier concentration due to indium doping. Further photoelectron spectroscopy experiments prove that In-doped NiPc is hole transport material.

Introduction

Electrical conductivity of phthalocyanine can be improved through doping with some dopant, for instance, oxidizing the ligands and creating an open shell, which results in the introduction of holes in the material [1]. The intercalation of alkali metal with metal phthalocyanine will enable electron-dope to the matrix. The Delf group demonstrated that thin films of transition metal phthalocyanines (MPcs), e.g. ZnPc, CuPc, NiPc, CoPc, FePc and MnPc initially insulating, can be turned into metallic through potassium intercalation (doping). Experimentally, they demonstrated that the doping dependent electrical conductivity of six different MPcs can be controlled their electron density by means of intercalation with alkali potassium atoms [2]. This electron-dope takes place due to the properties of alkali metals such as highly reactive at standard temperature and pressure, and readily lose their outermost electron.

We are interested if it is possible to utilize post-transition metal such as indium to intercalate with phthalocyanine to obtain hole doping. This is because post-transition metal atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell. Thereby, indium should be able to attract electrons from phthalocyanine molecule and create hole doping.

In the present research, NiPc is selected as the organic semiconductor material to intercalate with indium. The resulting properties of In-doped NiPc reveal that it is hole transport material.

Experiment

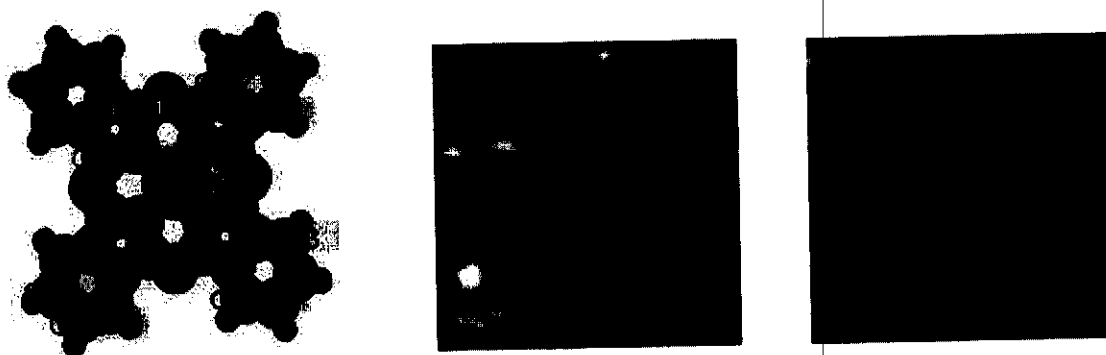
NiPc powder purchased from Aldrich was selected as the matrix material for the present study. Undoped NiPc and indium doped NiPc thin films were deposited by thermal evaporation method at a base pressure of 2×10^{-5} mbar. With indium dope, the molar doping ratio of indium and NiPc was specifically designed to be 1:4. The film thickness (100 nm) were continuously monitored during evaporation using two independent quartz crystal oscillators at a deposition rate of 0.4 nm/s for NiPc and 0.1 nm/s for indium. NiPc and indium were grown simultaneously on different three substrates: glass slide, silicon chip and transparent conductive indium tin oxide (ITO) coated glass slide. The film on glass slide substrate was given over to optical absorption measurement and the film on silicon substrate was deposited for surface morphology and crystalline characterization. The film on ITO glass substrate was fabricated as Schottky diode in order to measure its electrical characteristics because ITO electrode has proved to be an effective ohmic contact to many organic semiconductor

materials. Another electrode, the 100 nm thick aluminum electrode was deposited as Schottky contact by using thermal evaporation method as well. The completed devices had an effective area of approximately $2 \times 2 \text{ mm}^2$ for both pristine NiPc and In-doped NiPc. The structural studies of the films were carried out using X-ray diffractometer, whereas the atomic force microscope (AFM) measurements were performed to study their surface morphology and texture. To study the electrical characteristics of fabricated Schottky diode, the dark current-voltage ($I-V$) were recorded using Agilent precision LCR meter. UV-VIS optical absorption spectroscopy was used to measure a variation on optical property of undoped NiPc and In-doped NiPc samples.

Results and Discussions

Structural and surface morphology

The surface morphology of pristine NiPc and indium doped NiPc thin films on silicon substrates were determined by non-contact AFM as illustrated in Fig. 1. NiPc and In-doped NiPc films grown at room temperature have in both cases, a worm-like or a fiber-like structure, the same morphology. NiPc thin films usually are present in the NiPc α -phase in which NiPc molecules are standing almost upright in evaporated films and stack in a direction parallel to the substrate. The slight differences observed in pristine NiPc and In-doped NiPc is that the average grain size is slightly increased and the length of the fibers also increased upon doping with indium. This is because addition of indium cause a faster diffusion of NiPc molecules and therefore obtain a better ordering result in these worm-like crystallites. In other words, Although, there is intercalation of indium dopant on NiPc matrix with certain concentration ratio, its crystallinity is not drastically declined but remains more or less identical to that of pristine NiPc.



a) NiPc molecule. b) AFM image of undoped NiPc. c) AFM image of In-doped NiPc.

Fig.1. NiPc molecule and AFM images.

To analyze the arrangement of molecular crystal in the films, X-ray diffraction measurements of undoped NiPc film and In-doped NiPc film were performed as shown in Fig. 2. The diffraction peaks of both pristine NiPc and In-doped NiPc, are observed at $2\theta = 6.88^\circ$. These are related to the α -phase of NiPc. According to literature, its high intensity peak can be evaluated the reflection direction from [200] crystalline plane of NiPc. When NiPc is doped with indium, full width at half maximum (FWHM) of the diffraction peak is risen from 0.1999 to 0.2798 and lattice constant is gone up from 12.88 Å to 13.31 Å. This broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak which indicates that crystal lattice is increased. The significant increase in crystal plane spacing can be attributed to the formation of interlayer of NiPc molecules stacking plane and the layer of indium that penetrate between NiPc layer. Therefore, the fiber-like structure is seemed to be enlarged compared to that of pristine NiPc.

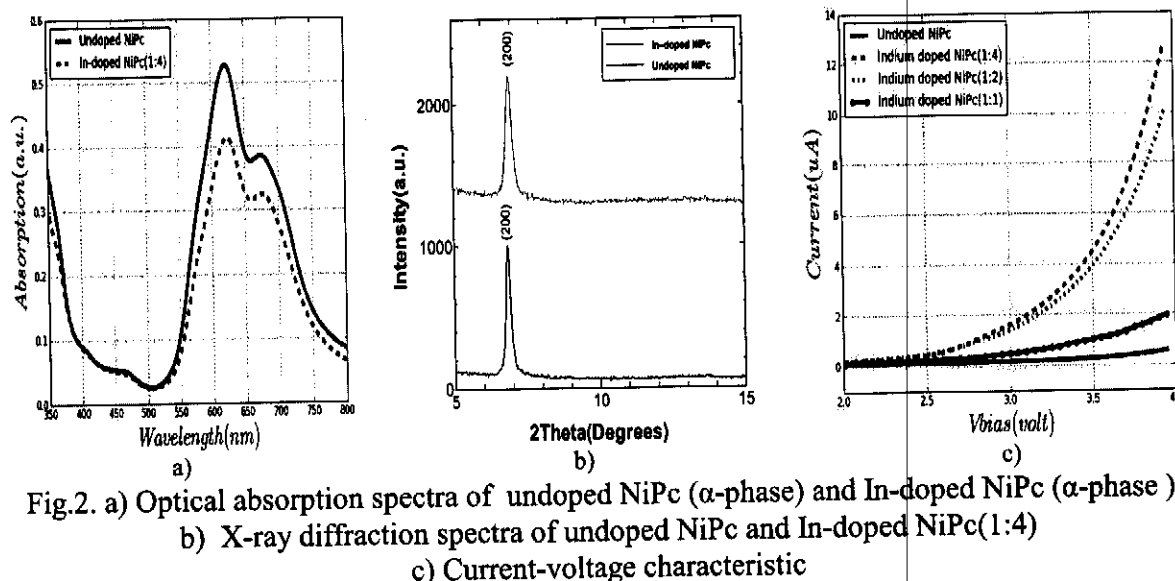


Fig.2. a) Optical absorption spectra of undoped NiPc (α -phase) and In-doped NiPc (α -phase),
 b) X-ray diffraction spectra of undoped NiPc and In-doped NiPc(1:4)
 c) Current-voltage characteristic

This observation is in agreement with the AFM images discussed above and indicates that no structural phase transition takes place when NiPc is doped with indium. However, it does not mean the formation of intercalated phases or new electronic phases do not exist. The doped phases of In-doped NiPc need to be studied in more detail further.

Optical absorption spectroscopy

Typically organic molecules of phthalocyanine and their derivatives have anomalous optical property as a result of their distinctive molecular ring structure. Optical transmission or absorption features can be used to distinguish the different modifications of phthalocyanine. Therefore, optical absorption spectra in the spectral region between 350 and 800 nm were recorded from both undoped NiPc film and In-doped NiPc film for comparison using a UV/VIS spectrophotometer as shown in Fig.2 a). Undoped NiPc thin film has two strong peaks appear at 340 nm and 620 nm, while the wavelength of the shoulder appear at 690 nm. The peak at 340 nm corresponds to the B absorption band, while the peak at 620 nm and 690 nm corresponds to the Q absorption band. The XRD peak at $2\theta = 6.88^\circ$ (Fig.2 b) and absorption spectrum of undoped NiPc thin film indicate that the pristine NiPc crystal structure is α -phase. With indium dope, its optical absorption intensity follow the same pattern as that of undoped NiPc and thereby, consistent with the crystal structure of α -phase.

Molecular crystal structure of NiPc was formed upon evaporation. It is known that, with different modifications, the structure vary with respect to the distance between the stacked molecules and the angle between the molecular axis and the stacking direction. These modifications exhibit typical absorption spectra and can be distinguished by using diffraction method. Not only the optical absorption spectra of both pristine NiPc film and In-doped film are more or less the same, but also their XRD peak both respond at $2\theta = 6.88^\circ$. No different diffraction was found, leading to conclusion that upon indium intercalation with certain concentration ratio (In:NiPc/1:4), does not cause significant changes in the crystal structure of the matrix material other than an increase in plane spacing of NiPc.

Current-voltage characteristic

A direct test of the effect of indium as a doping material in NiPc was carried out by measurements of the current as a function of applied voltage. Fig.3 c) shows typical current-voltage characteristics ($I-V$) of the ITO/NiPc/Al and ITO/In-doped NiPc/Al devices measured in the dark, at room temperature, and shows only under forward applied biasing voltage. Generally, the curves are similar to that of a metal/semiconductor (MS) Schottky barrier which is asymmetrical under forward and reverse

regions(not shown). This indicates that the space charge layer width in this structure is wide which support the thermionic of charge carriers through the wide barrier. In-doped NiPc device generate more current than that of pristine NiPc device indicates that it has more charge carrier concentration.

Photoelectron Spectroscopy Study

The basic principle of doping in organic semiconductor is equivalent to that in inorganic materials. Free charge carriers are generated by adding impurities which either transfer an electron to the electron conducting(LUMO) states(n-type doping) or remove electron from the hole conducting(HOMO) states(p-type doping). Generally, the type of semiconductor materials can be investigated by measuring the significant Fermi level shift towards the corresponding transport conducting states using photoelectron spectroscopy. For organic materials such as phthalocyanine, ultraviolet photoemission spectroscopy(UPS) is generally used to determine the HOMO peak position at binding energy of valence band emission. And inverse photoemission spectroscopy(IPES) is always used to investigate the LUMO peak position at binding energy of conduction band emission. Therefore, it requires both UPS and IPES to identify the type of doped organic semiconductor whether it is electron doped or hole doped material. However, x-ray photoemission spectroscopy(XPS) is going to be used to carry out investigation instead due to some reason.

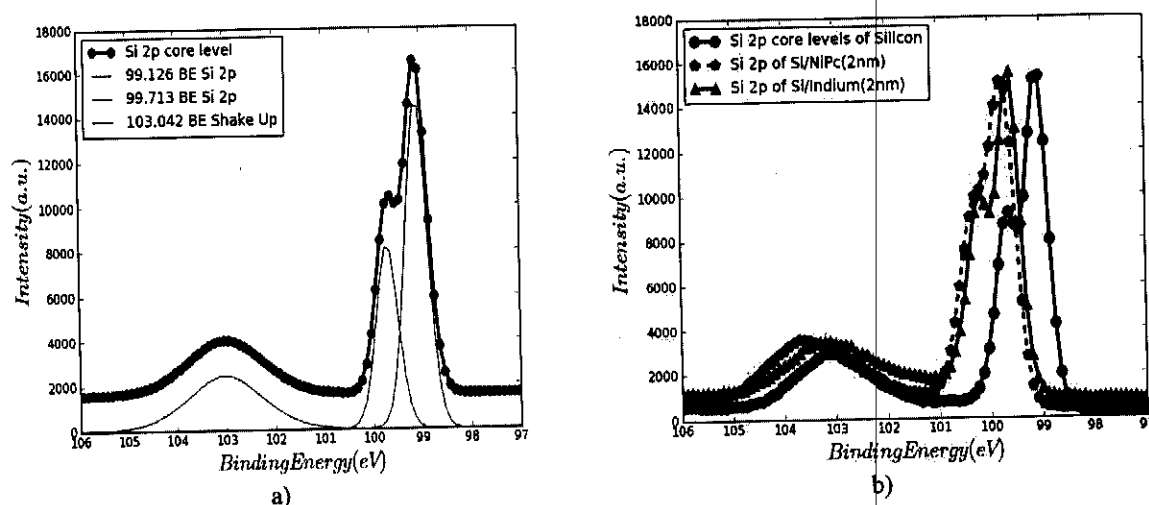


Fig.3. a) Si 2p core level XPS measurement of intrinsic Silicon substrate.
 b) Si 2p emission spectra of intrinsic Silicon substrate covered with indium compared to covered with pristine NiPc.

Fig. 3 a) shows the binding energies of Si 2p bulk component of the intrinsic silicon substrate used throughout the experiment. These peaks are due to the ejection of core level electrons by a direct interaction with the incident photon in which they composed of 99.126 eV, 99.713 eV components and the shake-up component at 103.042 eV. Energy splitting of a photoelectron peak is typically detected in an XPS spectrum, as a result of the interaction between the spins of the electron(up or down) and its orbital angular momentum. This interaction leads to a splitting of the degenerate state into 2 components. Thereby, the Si 2p electrons are split into 2 components with different binding energies i.e. Si 2p_{3/2} (99.126 eV) and Si 2p_{1/2} (99.713 eV). Since the Si 2p binding energy can vary for extremely n-doped to extremely p-doped samples between 98.8 eV and 99.9 eV, then, the physical interaction of phthalocyanine and intrinsic silicon at their interface should be observed directly from XPS spectrum of Si 2p. The cleaned intrinsic silicon substrates were used as the substrate for deposition of 2 nm thick undoped NiPc and the others, 2 nm thick In-doped NiPc to measure the shift of Si 2p emission spectrum due to the effect of Si substrate as depicted in Fig. 4. A 100 nm thick pristine NiPc film and 100 nm thick In-doped NiPc films also grown on the same type intrinsic silicon to investigate C 1s photoelectron spectrum and consequently confirm the existence of charge transfer between indium dopant and NiPc matrix.

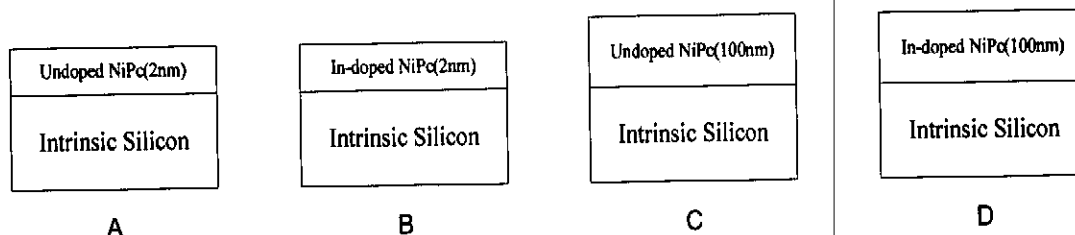


Fig.4. All different type of NiPc and In-doped NiPc deposited on the same type intrinsic silicon substrate.

A 2 nm thick NiPc film and 2 nm thick indium film were grown on the same type intrinsic silicon substrate and their Si 2p XPS spectra are illustrated in Fig. 3 b). Indium is a post-transition metal with 3 valence electrons, it does not react with water, boron, carbon and silicon. But indium can be intercalated into silicon and introduce conduction hole, forming a p-type silicon. During intercalation the indium atoms displace some of the bonded silicon atoms. With only 3 valence electrons, the hole in the bonding structure results in the intercalated sample being a p-type semiconductor. This hole doped silicon through interaction with indium at the interface can be noticeable on the displacement of Si 2p spectrum towards higher binding energy (BE) about 0.8 eV (up triangle mark line in Fig 3 b).

With the same manner as covered with indium, intrinsic silicon covered with NiPc(2nm), its Si 2p emission spectrum also move towards the higher binding energy direction. This indicates that pristine NiPc induces a p-type doping to intrinsic silicon as well. Phthalocyanine is known as a p-type organic semiconductor, thereby, there must be charge transfer between silicon substrate and NiPc molecules in such a way that electrons are attracted from silicon to NiPc molecules. This charge transfer must be further confirm through C 1s photoelectron spectrum. As shown in Fig. 3 b) and Table 1, Si 2p spectrum of Si/NiPc seemed to be shifted further than Si 2p spectrum of Si/In. Both indium and NiPc is capable of inducing intrinsic silicon to become hole doped silicon. If intercalation of indium into NiPc is achieved, then we can determine whether In-doped NiPc is hole doped semiconductor or electron doped semiconductor through the direction of the displacement of Si 2p emission spectrum (silicon substrate covered with In-doped NiPc thin film).

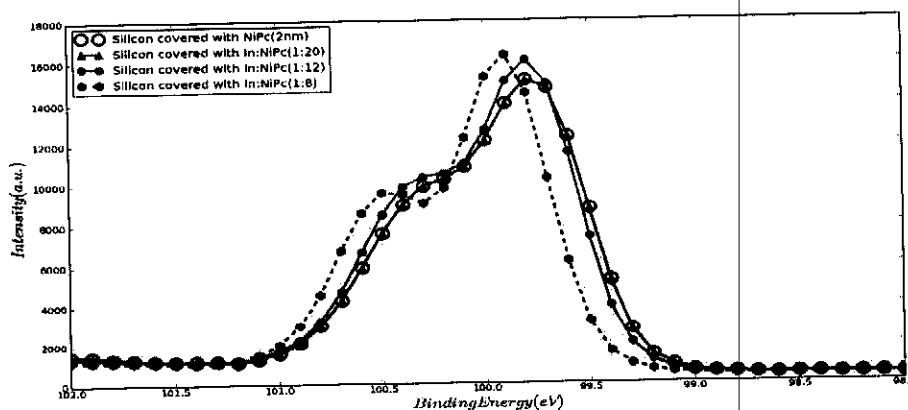


Fig.5. Si 2p core level XPS measurement of intrinsic Silicon covered with In-doped NiPc with different doping ratio.

Table.1. Si 2p core level components of XPS measurements in Fig. 5.

Type of silicon	Si 2p _{3/2}	Si 2p _{1/2}
Intrinsic silicon	99.106 eV	99.713 eV
Intrinsic silicon covered with Indium	99.632 eV	100.202 eV
Intrinsic silicon covered with NiPc	99.721 eV	100.220 eV
Intrinsic silicon covered with In:NiPc(1:20)	99.737 eV	100.227 eV
Intrinsic silicon covered with In:NiPc(1:12)	99.793 eV	100.347 eV
Intrinsic silicon covered with In:NiPc(1:8)	99.877 eV	100.487 eV

The Si 2p photoelectron spectrum of intrinsic silicon covered with In-doped NiPc(2nm) in which the ratio between indium and NiPc are 1:20, 1:12 and 1:8 are displayed in Fig. 5. With a slight doping ratio i.e. (1:20), The Si 2p spectrum of Si/In:NiPc(1:20) is almost overlapped with the spectrum of Si/NiPc(up triangle mark line and circle mark line). This indicates that their carrier concentration are not much different and their spectrum shift towards higher BE compared to spectrum of intrinsic silicon. In case of 1:12 doping ratio, its Si 2p spectrum move further to higher BE of 99.793 eV and 100.347 eV and with more doping ratio of 1:8, the Si 2p spectrum still shift further to higher BE of 99.877 eV for Si 2p_{3/2} and 100.487 eV for Si 2p_{1/2}. This particular shift of emission spectrum of Si 2p to higher BE of silicon substrate cover with In-doped NiPc suggest that silicon semiconductor at the interface is induced to be p-type semiconductor due to the effect of interfacing with indium doped NiPc. Consequently, In-doped NiPc should be hold transport material or hole dope organic semiconductor as same as pristine NiPc and it can induce intrinsic silicon to become p-type silicon in such a way that electrons from silicon are attracted to In-doped NiPc molecules.

But one might argue that since pristine NiPc is p-type semiconductor and both pristine NiPc and indium metal can induce intrinsic silicon to become p-type silicon at the interface[3], thereby, the shift of Si 2p spectrum to higher BE of Si/In:NiPc is the consequence of individual NiPc effect and the effect of indium separately at the interface. There might be no physical interaction between indium and NiPc or there is no charge transfer between indium and NiPc. However, with the current-voltage characteristic, it demonstrates that the carrier concentration of In-doped NiPc is increased according to the doping ratio. So, there must be charge transfer between indium and NiPc molecule in such a way that electrons from NiPc molecule are attracted to atoms of indium and NiPc becomes hole dope with indium intercalation. Thereby, we need more enough evidence to prove whether there is charge transfer between indium atoms and NiPc molecules. This problem can be investigated by studying the emission spectrum of C 1s electrons of NiPc[4].

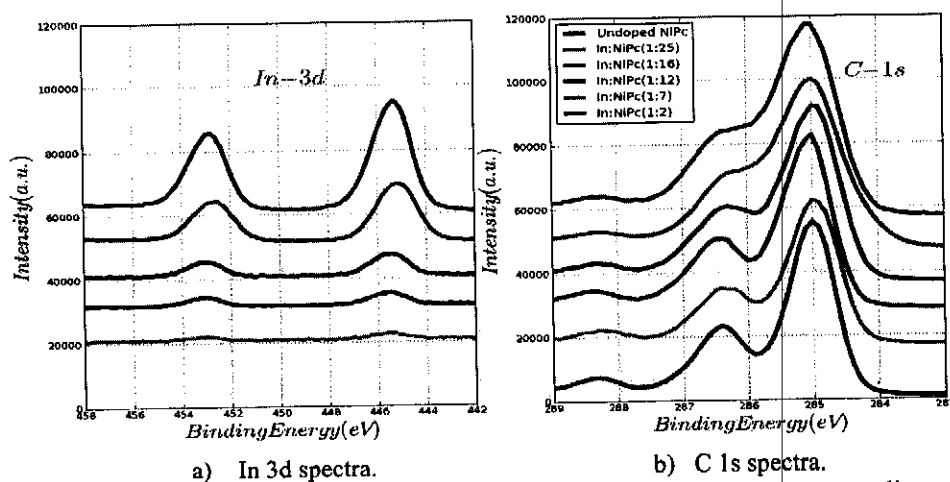
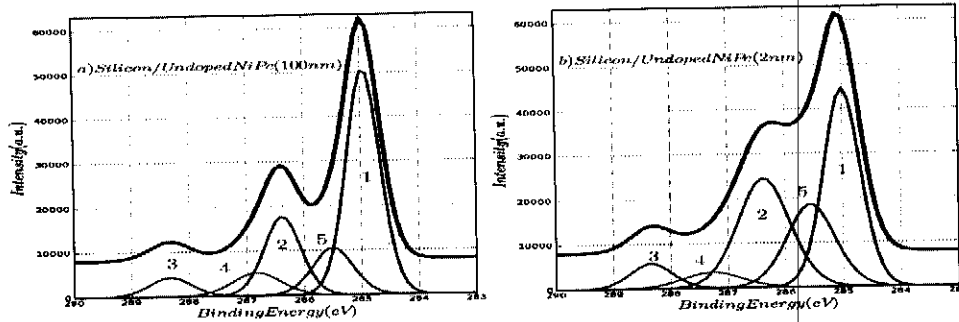


Fig.6. C 1s core level XPS spectra of pristine NiPc and In-doped NiPc according to increasing indium doping(In 3d)

To investigate if there is charge transfer between indium atoms and NiPc molecules, the XPS measurements of C 1s emission spectra have been carried out as shown in Fig. 6. The pristine NiPc film and indium intercalated NiPc films with various doping ratio deposited on silicon with 100 nm thick will be used in this study, in order to prevent the effect of silicon substrate, then a more thick film of 100 nm is required. The line shape of C 1s spectrum is changed regarded to the increase of indium dopant as illustrated in Fig. 6 b) in comparison with the risen of In 3d electrons of indium dopant as illustrated in Fig, 6 a). This noticeable change in line shape of C 1s spectrum with increasing indium dope demonstrate that the physical interaction of indium atoms and carbon atoms is existed certainly and happen in such a way that the charge transfer between indium atoms and carbon atoms of NiPc are electrons from 1s shell of carbon atoms are attracted to indium atoms and In-doped NiPc is hole dope as investigated by the shift of Si 2p spectra in Fig. 5.



a) C 1s spectrum of 100 nm thick pristine NiPc. b) C 1s spectrum of 2 nm thick pristine NiPc.

Fig.7. C 1s core level XPS measurement of pristine NiPc with and without the effect of silicon substrate.

The spectra of C 1s electrons from 100 nm thick In-doped NiPc in Fig. 6 reveal the charge transfer between indium and carbon atom in NiPc molecule and the spectrum of Si 2p electrons from Si/NiPc(2nm) and also Si/In:NiPc(2nm) indicates the effect of interfacing between silicon substrate and NiPc or In-doped NiPc, that is, there is the existence of charge transfer from silicon substrate to the bulk film. We can also use the C 1s emission spectrum to prove the happen of such a charge transfer. Fig. 7 shows the comparison of the C 1s spectrum of 100 nm thick pristine NiPc and the C 1s spectrum of 2 nm thick pristine NiPc in which the slight variation on C 1s line shape indicates the charges transfer from silicon atoms to NiPc molecules.

The C 1s core-level spectrum of phthalocyanine compose of the well-known three main spectral components(Fig.7 a). The highest peak, the component 1 is the result of electron photoemitted from the 24 aromatic carbon atoms of the four outer benzene rings(C2, C3, and C4 in Fig. 1. a) at about 284.97 eV. The second component(C-N) comes from the eight pyrrole carbon atoms linked to nitrogen(C1 in Fig. 1. a),at 286.387 eV. The weaker structure(component 3) stems from a two-electron process, known as a shake-up satellite of the pyrrole carbon atoms, involving a HOMO-LUMO transition and located at 288.301 eV. The introduction of component 4 which is an obscure satellite structure arising from the aromatic carbon(component 1) and hidden under component 2, improves the agreement of the expected intensity ratio between aromatic carbon and pyrrole carbon of 3:1. This component 4 occurs at 286.847 eV under component 2 and is a shake-up satellite associated to carbon atom in benzene rings. The last component 5 which its origin is less evident or it is still not fully understandable, is needed to get the results of the fit close to the expected value of 3, the ratio number of C atoms in benzene rings and pyrrole rings.

Recently, the origin of component 5 has been explained that the component 5 peak is attributed to the excitation of the in-plane C-H stretch vibrational mode associated to electron emission from C 1s level, as also suggested by a recent work on lead phthalocyanine[5]. This hypothesis is consistent with the results of the fit.

Table.2. Numerical results from the C 1s fit shown in Fig.7.

Peak	BE(eV)	FWHM	Area(%)
C 1s components of NiPc(100nm)			
1. Main line C-C	284.970	0.667	53.5
2. Main line C-N	286.387	0.721	20.0
3. Shake-up C-N	288.301	0.847	5.6
4. Shake-up C-C	286.847	0.955	7.6
5. Vibrational coupling C-H	285.483	0.801	13.2
C 1s components of NiPc(2nm)			
1. Main line C-C	284.979	0.726	38.4
2. Main line C-N	286.363	1.034	29.9
3. Shake-up C-N	288.331	0.837	5.6
4. Shake-up C-C	287.278	1.169	4.9
5. Vibrational coupling C-H	285.553	0.966	21.1

A point of comparison between NiPc film in solid phase(100nm) and NiPc film in submonolayer phase(2nm) which is influenced by the presence of silicon substrate, can be facilitated through the change of line shape of C 1s emission spectrum in Fig.7 b) contrasted with the line shape of C 1s emission spectrum in Fig. 7 a). The C 1s spectrum of NiPc(100nm) composed of three main peaks as mentioned earlier and the valley between the main peaks is deeper. This spectrum is due to NiPc in its standard solid phase, that is, molecules are no longer influenced by the presence of silicon substrate and all its five fitting components are reported in table 2. The clear contrast between the two spectra are the absence of the valley between the benzene ring peak and pyrrole ring peak in the submonolayer phase(2nm), the energy distance between the two main peaks and the ratio between benzene ring peak and pyrrole ring peak. The curve fitting analysis of spectrum corresponding to submonolayer phase and bulk-like phase in Fig. 7 and table 2 provide evidence relating to the nonappearance of the valley, that is, the intensity of component 5 is significantly increased which is a direct consequence of charge transfer from silicon substrate.

Generally, the intensity of component 5 will be higher risen if phthalocyanine is intercalated with some dopant whether electron dope or hole dope, for instance, copper phthalocyanine(CuPc) intercalated with potassium(electron dope) and zinc phthalocyanine(ZnPc) intercalated with indium in which we expect to be hole dope. With curve fitting, the significant change of line shape of C 1s emission spectrum of indium doped NiPc in solid-phase(100nm) in Fig. 6 b), indicates the interaction between indium and carbon atom of NiPc which is also interpreted as the increase of component 5(not shown). Thereby, the fifth spectral component(C-H vibrational coupling) of C 1s spectrum of NiPc increase upon indium doping and as well as, the effect of silicon substrate. The variation on C1s spectral line shape of submonolayer-phase NiPc on silicon substrate and the shift of Si 2p spectrum to higher BE demonstrate the physical interaction between silicon atoms and NiPc molecules in such a way that NiPc which is p-type organic semiconductor can change intrinsic silicon into p-type silicon at the interface.

Even though, both the effect of silicon substrate and intercalation with indium can cause significant change of C 1s spectral line shape of NiPc film and the intensity of component 5 increase considerably. However, with C 1s spectra evolution of indium intercalated NiPc with various doping ratio but not more than 1:2 as shown in Fig. 6 b), surprisingly, the intensity of the fifth spectral component never over and above the intensity of the second spectral component(pyrrole peak). Then, the submonolayer-phase In-doped NiPc(2nm) film on intrinsic silicon should exhibit something distinctly different from Si/pristine NiPc(2nm) according to the effect of both silicon substrate and indium intercalation.

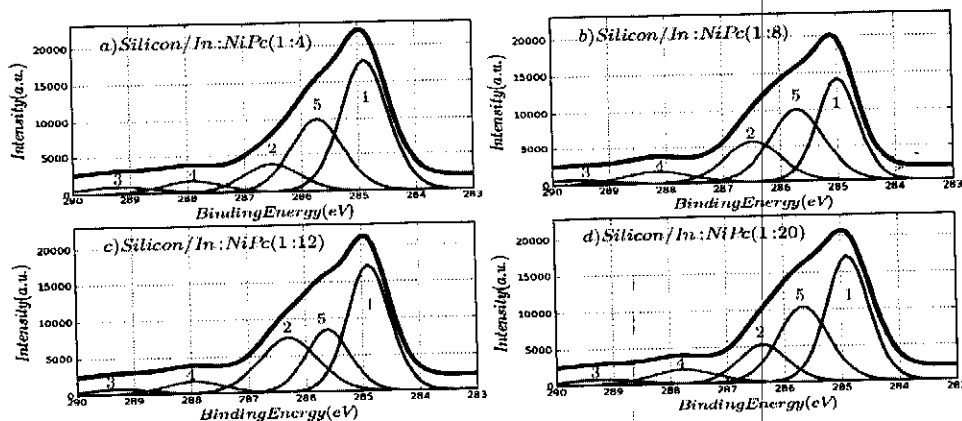


Fig.8. C 1s core level XPS measurement of submonolayer-phase indium intercalated NiPc with effect of Si substrate

Fig. 8 shows evolution of line shape of C 1s emission spectra of In-doped NiPc(2nm) on intrinsic silicon substrate. The intercalation ratio between indium and NiPc is varied from slight dope to heavy dope including 1:20, 1:12, 1:8 and 1:4. All of the C1s spectral line shape of In-doped NiPc(2nm) on

intrinsic silicon are very different from that of pristine NiPc on intrinsic silicon (Fig. 7b). That is, we cannot notice the appearance of the second spectral component (pyrrole peak) from the line shape, because the fifth spectral component is risen beyond the intensity of the second peak which associated to pyrrole carbon atoms in all cases of doping ratio. The occurrence of such an over intensity of the fifth spectral component indicates the influence of silicon substrate to In-doped NiPc film and can be interpreted as there is interaction between silicon atoms and In-doped NiPc molecules as well as in case of pristine NiPc. This finding and the shift of Si 2p spectrum of intrinsic silicon covered with In-doped NiPc (2nm) towards higher BE which is proportional to the amount of indium doping ratio confirm that In-doped NiPc can turn intrinsic silicon into p-type silicon and direction of the shift demonstrates that In-doped NiPc is p-type organic semiconductor or hole transport material. In other words, intercalation of indium into NiPc is hole doping.

Summary

The intercalation of indium into NiPc induce higher charge carrier concentration which is proportional to increasing doping ratio. The displacement of Si 2p XPS spectrum towards higher binding energy of intrinsic silicon substrate covered with pristine NiPc indicates that NiPc is p-type semiconductor. Submonolayer-phase 2nm thick indium intercalated NiPc film on intrinsic silicon substrate causes the Si 2p emission spectrum shift in the direction of higher BE which is directly proportional to indium doping ratio, that is, In-doped NiPc is p-type as well. This finding reveals the presence of interaction of silicon atoms and In-doped NiPc molecules at the interface and automatically implies that there must be charge transfer from silicon to In-doped NiPc. The considerable increase of C-H vibrational coupling spectral component of C 1s XPS spectrum of In-doped NiPc (2nm) on silicon substrate confirms the existence of charge transfer from silicon to In-doped NiPc thin film and support the resulting reposition of Si 2p spectrum. The significant change of line shape of C 1s spectrum of In-doped NiPc in bulk-like phase (100nm) indicates that intercalation of indium into NiPc film bring about charge transfer to carbon atoms in NiPc molecules. With Si 2p XPS results, NiPc intercalated with indium dopant is hole dope organic semiconductor or hole transport material.

Acknowledgments

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