

Preparation and Vacuum-Ultraviolet Photoemission of Evaporated Thin Films of Metal(II) Glyoximate Complexes

Naoki Sato

Thin films of metal(II)(Ni, Pd and Pt) complexes of glyoxime derivatives, *i.e.*, bis(glyoximate)metal(II), have been prepared by vacuum deposition. X-ray diffraction, electronic absorption, photoelectron spectra and electric resistivities of these films have been measured. Various molecular orientations in the films are observed for different metals or ligands. The lowest absorption energies show the same order of magnitude as the threshold ionization energies from Ni to Pt complexes in most cases. Several films can be grouped into the narrow gap semiconductors.

Keywords: Bis(glyoximate)metal(II)/ Thin film/ Molecular orientation/ Electronic structure/ Narrow gap semiconductor

Most of planar molecular complexes of group ten metals coordinated by two molecules of glyoxime derivatives (Rgly), $M(Rgly)_2$ ($M = Ni, Pd \text{ and } Pt$), stack in the manner that their d_{z^2} orbitals of d_8 metal ions overlap with each other, so that their crystal structures are characterized by one-dimensional arrangements of metal ions in the direction perpendicular to the molecular plane. We have tried to prepare evaporated thin films of these molecules and to examine structures and properties of the obtained films, in particular, their valence electronic structures using ultraviolet photoemission measurements.

Materials studied in this work were group ten metal complexes of glyoxime derivatives as follows: dimethylglyoxime (dmg), diphenylglyoxime (dpg), diaminoglyoxime (dag), 1,2-cyclohexanedione dioxime or nioxime (niox), 1,2-benzoquinone dioxime (bqd), 1,2-acenaphthenequinone dioxime (anqd), 9,10-

phenanthrenequinone dioxime (paqd). These ligand molecules were synthesized and the metal complexes were prepared by mixing the hot water-alcohol solutions containing stoichiometric amounts of a metal salt ($NiCl_2$, K_2PdCl_4 or K_2PtCl_4) and a ligand, respectively. The final products were purified by repeated recrystallization from *e.g.*, *N,N*-dimethylformamide or *o*-dichlorobenzene. Chemical composition of all materials used were confirmed by elemental analysis.

Thin film preparation of $M(Rgly)_2$ ($M = Ni, Pd, Pt$) was tried by vacuum deposition onto a quartz-glass or a polycrystalline copper substrate held at room or a regulated temperature using a low heat capacity evaporation source in vacuum where the pressure was about 1.33×10^{-4} Pa [1]. Thermal decomposition of most materials in the source was competed with their film deposition, especially at a deposition rate

INTERFACE SCIENCE — Molecular Aggregates —

Scope of research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric behaviors. The electronic structure of molecular and/or polymeric thin films is studied in connection with the former, and its results are applied to create novel molecular systems with characteristic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.



SATO

ASAMI

KITA

SEKINE

Professor

SATO, Naoki (D Sc)

Associate Professor

ASAMI, Koji (D Sc)

Instructors

KITA, Yasuo (D Sc)

SEKINE, Katsuhisa (D Sc)

Students

ENDO, Sotaro (MC)

KAWAMOTO, Ikuko (MC)

KOIDE, Norihiro (MC)

MATSUBARA, Akira (MC)

ODA, Masao (DC)

no more than 0.2 nm/min. Only $M(dag)_2$ did not give a film even at a rate much higher than 0.2 nm/s. The thicknesses of films obtained for the complexes of the other six kinds of ligands, monitored by a quartz oscillator, were ranged from 50 to 150 nm. X-ray diffraction profiles, electronic absorption spectra, ultra-violet photoemission spectra [2] and electric resistivities of the complex films were measured in most cases at room temperature to study characteristics of their structural and electronic properties.

Molecular orientations in the films have been examined to be dependent on the compound and/or deposition conditions, in particular, the substrate. For example, on a quartz-glass substrate, a $Ni(bqd)_2$ film is amorphous, while $Pd(bqd)_2$ and $Pt(bqd)_2$ films are uniaxially oriented [3]. Further, a $Pt(dmg)_2$ film is oriented with the molecular stacking axis parallel to a quartz-glass surface, whereas perpendicular to a graphite surface. The lowest electronic absorption energies, assigned to the electronic transitions from nd_{z^2} to $(n+1)p_z$ levels for Pd and Pt complexes in most cases, show the same order of magnitude as their threshold ionization energies from Ni to Pt complexes

in most films. The $Pt(bqd)_2$ film shows the lowest value of the transition energy 0.99 eV in all the compounds measured in this work. Its threshold ionization energy 4.96 eV is as small as the lowest values ca. 4.8 eV for $Pt(niox)_2$ and $Pd(anqd)_2$ films. Thus, these data as well as the results of electric resistivity measurements lead to a conclusion that several films above can be grouped into the narrow gap semiconductors of molecular origin.

This work has partially been carried out in cooperation with Profs. I. Shirotani (Muroan Inst. Tech.), M. Yamashita (Nagoya Univ.) and S. Kitagawa (Tokyo Metropol. Univ.). The author thanks K. Ono (Univ. Tokyo) for collaboration in part.

References

1. N. Sato, K. Seki and H. Inokuchi, *Rev. Sci. Instrum.*, **58**, 1112 (1987).
2. E.g., N. Sato, Y. Saito and H. Shinohara, *Chem. Phys.*, **162**, 433 (1992).
3. I. Shirotani, T. Kudo, N. Sato, H. Yamochi and G. Saito, *J. Mater. Chem.*, **5**, 1357 (1995).

Electrical Properties of Peptaibol-induced Ion-channels in Bilayer Lipid Membranes

Koji Asami, Norihiro Koide and Akira Matsubara

Peptaibols are antibiotic peptides, some of which produce voltage dependent ion-channels in bilayer lipid membranes (BLM). In this report we describe the electrical properties of ion-channels formed in planar bilayer lipid membranes by trichocellin and template-assembled alamethicins.

Keywords: Single-channel recording/ Template-assembled synthetic peptide/ Trichocellin/ Alamethicin

Peptaibols are a family of antibiotic peptides that contain α -aminoisobutyric acid residues and have an α -aminoalcohol at the C-terminal. Alamethicin, an extensively studied peptaibol, forms voltage-dependent ion-channels in BLM. The electrical properties of the channels are interpreted in terms of a barrel-stave model, a bundle of parallel helices spanning BLM. Studies of the ion-channels formed by peptaibols, which is much simpler in structure than ion-channel proteins, would provide useful knowledge on the relationship between the ion-channel structure and function. In this study, we focus on the electrical properties of the ion-channels formed in planar BLMs by trichocellin and template-assembled alamethicins (called ALn -cyclo $2n$) that have been prepared by linking n alamethicin monomers to a cyclic pseudopeptide, cyclo(Lys-mAbz) n .

Trichocellin formed ion-channels with several discrete conductance states corresponding different pore sizes. The low-conductance state channels showed nonlinear current-voltage curves, which may result from the interaction between ions and the pore wall.

All the channels observed with KCl solutions were slightly cation-selective. The order of ion selectivity among alkali metal cations was $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ with 3 M chloride salt solutions. The selectivity order is close to the mobility sequence for the ions in aqueous solution, suggesting that the channels behave as a water-filled pore and the ions pass through the channels in hydrated form.

For template-assembled peptides, it would be expected that one peptide molecule produces one ion-channel with a definite pore size and that the channel has a long open lifetime. All the tree ALn -cyclo $2n$ peptides ($n=3-5$) formed long-lived channels. The unitary conductances of the $AL3$ -cyclo 6 ($n=3$) and $AL4$ -cyclo 8 ($n=4$) channels were in agreement with the lowest and the next lowest conductances of the alamethicin channel, respectively, whereas the $AL5$ -cyclo 10 channel had various conductance states. This finding may imply that the structural rigidity of the template peptides is one of the important factors in determining the ion-channel properties.