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REVIEW

Organometallic chemistry related to applications for microelectronics in Japan

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This is meant to be a brief overview of the developments of research activities in Japan on organometallic compounds related to their use in electronic and optoelectronic devices.

The importance of organometallic compounds in the deposition of metal and semiconductor films for the fabrication of many electronic and optoelectronic devices cannot be exaggerated. Their scope has now extended to thin-film electronic ceramics and high-temperature oxide superconductors. A variety of organometallic compounds have been used as source materials in many types of processing procedures, such as metal–organic chemical vapor deposition (MOCVD), metal–organic vapor-phase epitaxy (MOVPE), metal–organic molecular-beam epitaxy (MOMBE), etc. Deposited materials include silicon, Group III–V and II–VI compound semiconductors, metals, superconducting oxides and other inorganic materials.

Organometallic compounds are utilized as such in many electronic and optoelectronic devices; examples are conducting and semiconducting materials, photovoltaic, photochromic, electrochromic and nonlinear optical materials.

This review consists of two parts: (I) research related to the fabrication of semiconductor, metal and inorganic materials; and (II) research related to the direct use of organometallic materials and basic fundamental research.

Keywords: Microelectronics, optoelectronics, semiconductors, metals, MOCVD, MOVPE, MOMBE, photochemistry, metal complexes, organometallic polymers

The importance of organometallic compounds in the deposition of metal and semiconductor films for the fabrication of many electronic and optoelectronic devices cannot be exaggerated.[1–3] Their scope has now extended to thin-film electronic ceramics and high-temperature oxide superconductors.[4] A variety of organometallic compounds have been used as source materials in many types of processing procedures, such as metal–organic chemical vapor deposition (MOCVD), metal–organic vapor phase epitaxy (MOVPE), metal–organic molecular-beam epitaxy (MOMBE), etc. Deposited materials are silicon, Group III–V and II–VI compound semiconductors,* metals, superconducting oxides and other inorganic materials. From the viewpoint of organometallic chemists, who make every effort to synthesize many new compounds which are nonexistent in nature, it may seem wasteful to decompose them again to obtain metal components. However, this produces a variety of highly efficient and also highly valuable devices which are essential to human life in the contemporary age. On the other hand, organometallic compounds are utilized as such in many electronic and optoelectronic devices. Conducting and semiconducting materials, photovoltaic, photochromic, electrochromic and nonlinear optical materials are a few such compounds utilized in these devices.

This paper is meant to give a brief overview of the developments of research activities in Japan on organometallic compounds related to their use in electronic and optoelectronic devices. The coverage is, of course, far from complete. The present Reviewer is afraid that many important works may have been inadequately treated or even inadvertently neglected, and he apologizes to the authors of those works. Naturally, many of the achievements in Japan have been made following on, or keeping pace with, discoveries and innovations which have been made outside Japan. Because of the nature of the present Review, however, reference is made only to research activities in Japan, except for a few pioneering

* The latter two should be called Group 13–15 and 12–16 compound semiconductors under the 18 groups notation currently recommended by IUPAC. However, they are still called Group III–V and II–VI in the contemporary electronics communities. Therefore, the present Reviewer has adhered to the older notations in this review.

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and collective works which have been carried out outside Japan. It is characteristic of this field of research that the demands from the industrial side have kept to give a large impetus to the fundamental research, since the practical applications are directly connected to the industrial production of many kinds of materials and devices. The present Review consists of two parts, (I) research related to the fabrication of semiconductor, metal and inorganic materials, and (II) research related to the direct use of organometallic materials and basic fundamental research. Interestingly, the former research in Japan has been performed mostly by people in electronic disciplines and by people in industry. Chemists have been engaged mostly in research related to the direct use of organometallic compounds and more basic fundamental research. These characteristics are partially reflected in the papers which are collected in this issue.

PART I: RESEARCH RELATED TO FABRICATION OF SEMICONDUCTOR, METAL AND INORGANIC MATERIALS

This Part gives a quick look at the developments in Japan of the research related to these fields.

There are several types of processing procedures in which organometallic compounds are utilized. In metal–organic chemical vapour deposition (MOCVD), metal or semiconductor films are deposited by the dissociation of gaseous organometallic compounds upon some solid substrate. The energy input for the rupture of organometallic bonds is given by heat (in conventional, thermal MOCVD), by plasma (in plasma MOCVD), or by light (in photo-MOCVD or laser MOCVD). Following pioneering works by Manasevit,[5,6] a remarkably large number of investigations has been performed. The MOCVD technique has its merit in inexpensive preparation of large-area thin films, doping control, and fabrication of multilayer structures. Compared with conventional (thermal) MOCVD, photo- and laser MOCVD have the merit of processing at relatively low temperatures. It also enables maskless 'dirct writing' to the light diffraction limit. In the fabrication of Group II–VI and III–V compound semiconductor films, epitaxial growth on a substrate (e.g. ZnSe on GaAs) is essential. The metal–organic vapour-phase epitaxy (MOVPE) technique has been widely used for this purpose. In the preparation of Group II–VI compound semiconductors, Group II source materials, e.g. dimethylzinc [$Zn(CH_3)_2$], and Group VI source materials, e.g. diethylselenide [$Se(C_2H_5)_2$], are separately introduced into the reaction chamber because they are prone to cause parasitic reactions in the gas phase. In the conventional fabrication of Group III–V semiconductors source gases of Group III and Group V are introduced at the same time. In atomic layer epitaxy (ALE), however, source gases of Groups III and V are supplied alternately, avoiding mixing in the gas phase. A self-limiting mechanism, in which crystallization automatically stops with the completion of one (or *n*)-layer coverage, is essential in ALE. Molecular beam epitaxy (MBE) is distinct from other techniques in that the reactants are introduced in a molecular beam under a very low (e.g. $\sim 10^{-10}$ atm; 7.6×10^{-8} Torr) working pressure. Metal–organic MBE (MOMBE) uses gaseous organometallic compounds in MBE; this eliminates the problem of crucibles used in conventional MBE. It also enables selective deposition, multilayer fabrication and very high doping. The successful fabrication of many sophisticated layered structures, such as a AlGaAs/GaAs double heterostructure (DH) laser by Dupuis *et al.*,[7–10] gave a great stimulus to MOCVD and MOVPE techniques. Suntola *et al.*[11] reported ALE production of Group II–VI compound semiconductors using conventional MBE equipment. Veuhoff[12] reported the first MOMBE using trimethylgallium [$Ga(CH_3)_3$] and arsine.

The following compounds are commonly used: $Zn(CH_3)_2$ dimethylzinc, $Zn(C_2H_5)_2$ diethylzine, $Al(CH_3)_3$ trimethylaluminum, $Al(C_2H_5)_3$ triethylaluminum, $Ga(CH_3)_3$ trimethylgallium, $Ga(C_2H_5)_3$ triethylgallium, $In(CH_3)_3$ trimethylindium, $In(C_2H_5)_3$ triethylindium, $S(C_2H_5)_2$ diethyl sulfide, $Se(CH_3)_2$ dimethyl selenide, $Se(C_2H_5)_2$ diethyl selenide, $As(C_2H_5)_3$ triethylarsenic, and $Sb(C_2H_5)_3$ triethylantimony.

Silicon

Although silane (SiH_4) and disilane (Si_2H_6) used for preparation of silicon are not organometallic compounds, a few words on the photo-CVD of silicon may be relevant here, considering the vital importance of silicon in present-day electronics technology.

Kumagawa *et al.*[13] reported an attempt to examine the effect of photoirradiation during vapor-phase epitaxial growth of silicon films.

Hanabusa *et al.*[14] deposited silicon films by irradiating silane with a pulsed carbon dioxide (CO_2) laser. The laser-induced vapor deposition occurred effectively when the laser was tuned to an absorption frequency of silane. Mishima *et al.*[15] reported the deposition of amorphous α-Si : H films by direct photolysis of disilane by low-pressure mercury lamps. Hanabusa *et al.*[16] prepared α-Si : H films using a CO_2 laser. Urisu and Kyuragi[17] reported photoexcited CVD of a silicon nitride film using synchrotron radiation. Kizaki *et al.*[18] synthesized and characterized Si_3N_4 powder from an NH_3/SiH_4 system by CO_2 laser irradiation. Hada's group[19,20] studied the nucleation in the very early stage of photo-CVD of amorphous silicon from disilane on a silicon dioxide substrate using a chemical amplification technique to detect small silicon nuclei. They found two different regions of substrate temperature; in the low-temperature region up to about 150 °C, the initial nucleation rate decreased as a whole with substrate temperature, whilst above 150 °C the tendency was apparently reversed suggesting a change of nucleation mechanism. They discussed basic surface reactions possibly involved in the nucleation step.

Group III–V compound semiconductors

Saitoh and Minagawa[21] reported in 1973 epitaxial growth of $GaAs_{1-x}P_x$ for electroluminescent diodes using $Ga(CH_3)_3$, arsine and phosphine. However, the history of MOCVD growth of Group III–V compound semiconductors, especially GaAs, is characterized with the long, persisting demand for highly purified starting materials (organometallic compounds), in order to obtain films of high electron mobility and low impurity (unintentionally doped carriers) concentration, as briefly summarized below. Ito *et al.*[22] detected a large quantity of impurities such as silicon, carbon and others in the deposited layer of GaAs. Silicon or carbon mainly came from $Ga(CH_3)_3$. Nakanisi *et al.*[23] also remarked on the vital importance of the purity of $Ga(CH_3)_3$ in the MOCVD of GaAs using $Ga(CH_3)_3$ and arsine. Takagishi and Mori[24,25] studied the effects of operating pressure and arsine/$Ga(CH_3)_3$ ratio on the electric properties of undoped GaAs epitaxial layers grown by low-pressure MOCVD (3×10^{-3} to 75 Torr). The conductivity of the epitaxial layers grown under the same arsine/$Ga(CH_3)_3$ ratio (75) changed from p-type to n-type at 5×10^{-1} Torr as operating pressure was increased. Carbon from $Ga(CH_3)_3$ was the dominant acceptor (i.e. p-type impurity) and its concentration decreased as the operating pressure was increased. The increase of arsine/$Ga(CH_3)_3$ ratio at a constant pressure (8 Torr) caused the switchover from p-type to n-type. Tokumitsu *et al.*[26] reported MOMBE of GaAs using $Ga(CH_3)_3$ and As_4 molecular beams. The epitaxial layers grown showed p-type conduction, with a high carrier concentration (10^{18}–10^{19} cm^{-3}) due to residual carbon. Hata *et al.*[27] studied the residual impurities in GaAs and AlGaAs grown using $Ga(CH_3)_3$, $Al(CH_3)_3$ and arsine. It was concluded that the purity of GaAs layers was determined by the donors, germanium and silicon, associated with arsine, and the carbon acceptor from $Ga(CH_3)_3$. The quality of AlGaAs layers was found to be influenced by these impurities such as methoxide ($—OCH_3$) in $Al(CH_3)_3$, and still more influenced by oxygen in arsine.

Trimethyl organometallics are thus known to result in high carbon incorporation into grown layers. Triethyl organometallic compounds such as $Ga(C_2H_5)_3$ and $Al(C_2H_5)_3$ reduced the carbon contamination remarkably in AlGaAs grown by MOCVD.[28] Actually, the use of $Ga(C_2H_5)_3$ was proposed earlier by Seki *et al.*,[29] who used it with arsine (1 % in Ar) to obtain GaAs epitaxial layers of high mobility. Tokumitsu *et al.*[30] reported MOMBE growth of GaAs using $Ga(C_2H_5)_3$ in comparison with $Ga(CH_3)_3$. Using $Ga(C_2H_5)_3$ as a gallium source, epitaxial layers grown at temperatures below 580 °C showed n-type conduction and a carrier concentration of about 1×10^{17} cm^{-3}, whilst those grown at higher temperature showed p-type conduction. Introduction of ionized hydrogen into the $Ga(CH_3)_3$–As_4 system reduced the carrier concentration from 1×10^{20} cm^{-3} to 1×10^{18} cm^{-3}. Kondo *et al.*[31] prepared high-quality GaAs by MOMBE using $Ga(C_2H_5)_3$ and metallic arsenic. An unintentionally doped GaAs layer exhibited p-type conduction with the carrier concentration as low as 8×10^{14} cm^{-3} (room temperature). The carrier concentration obtained in GaAs was the lowest reported by gas-source MBE or MOMBE at that time.

Surface morphology is very important in device applications. MOMBE eliminated large (>10 μm) surface defects found in MBE using metallic gallium. Ishikawa *et al.*[32] studied surface morphology of GaAs on a (100) GaAs substrate grown by MOMBE using $Ga(CH_3)_3$ and arsenic (As_4). Surface morphology was found to depend strongly on growth temperatures (550–700 °C)

and $As_4/Ga(CH_3)_3$ beam intensity ratio (0.5–10). After optimization of the growth parameters ($T_{sub}=600$ °C, ratio = 1), there were only two kinds of defects and defect density was reduced to 21 cm^{-2} for defects larger than 5 μm in diameter.

Arsine is highly toxic. The common impurities in arsine are water and oxygen, and both cause a serious effect, as Terao and Sunakawa[33] probed by photoluminescence of prepared AlGaAs. Alkylarsenic is less reactive with water, and much less toxic than arsine. Fujita *et al.*[34] reported MOVPE of GaAs using $Ga(CH_3)_3$ and $As(C_2H_5)_3$. Incorporation of carbon from $As(C_2H_5)_3$ degraded electrical properties.

Reaction mechanisms in the formation of GaAs were studied by several groups. Nishizawa and Kurabayashi[35] investigated the reaction mechanisms of MOCVD of GaAs with infrared absorption spectroscopy. In the $(Ga(CH_3)_3 + AsH_3 + H_2)$ system, they found a new band at 2080 cm^{-1} which was not observed in either $(Ga(CH_3)_3 + H_2)$ or $(AsH_3 + H_2)$, indicating some intermediate formation. They reported that the decomposition of arsine was affected strongly by the addition of $Ga(CH_3)_3$. Yoshida *et al.*[36] studied decomposition of $Ga(CH_3)_3$ and $Ga(C_2H_5)_3$ in hydrogen (H_2) and nitrogen (N_2) atmospheres. The reaction mechanisms were hydrogenolysis for $Ga(CH_3)_3$ in H_2, homolytic fission for $Ga(CH_3)_3$ in N_2, and β-elimination for $Ga(C_2H_5)_3$ in both H_2 and N_2.

Mashita *et al.*[37] studied how the pyrolysis of $Ga(C_2H_5)_3$ on a GaAs wafer was affected by the presence of arsine or $Al(CH_3)_3$. An *in-situ* analysis of the ambient gas in a low-pressure MOVPE reactor was made using a quadrupole mass spectrometer. The addition of arsine lowered the $Ga(C_2H_5)_3$ pyrolysis temperature and resulted in the formation of ethane and ethylarsines ($(C_2H_5)_nAlH_{3-n}$, $n = 1$–3). The formation of ethyl radicals and the reaction between ethyl radicals and arsine were indicated. The addition of $Al(CH_3)_3$ to $Ga(C_2H_5)_3$ raised the $Ga(C_2H_5)_3$ pyrolysis temperature. Mass spectra for the $Ga(C_2H_5)_3$–$Al(CH_3)_3$–H_2 system showed the presence of ion species $CH_3(C_2H_5)_2Ga^+$. They suggested the production of mixed alkyls [$(CH_3)_n(C_2H_5)_{3-n}Ga$, $n = 1, 2$) through the rapid exchange of alkyl groups due to the equlibrium between dimer and monomer. Tsuda *et al.*[38] carried out an *ab initio* molecular orbital calculation. It was shown that the combination of radical mechanism for $Ga(CH_3)_3$, $Ga(CH_3)_3 \rightarrow Ga(CH_3)_2^{\cdot} + CH_3^{\cdot}$ and the molecular mechanism for $Ga(C_2H_5)_3$, $Ga(C_2H_5)_3 \rightarrow GaH(C_2H_5)_2 + C_2H_4$, explained qualitatively the experiments on the pyrolysis temperatures of $Ga(CH_3)_3$ and $Ga(C_2H_5)_3$ in the MOCVD growth reactor.

Selective growth of GaAs (preparation of crystal on some part of the substrate surface) receives much attention as a promising technique for achieving monolithic integration of electronic and optoelectronic devices. Nakai and Ozeki[39] reported selective deposition of GaAs on a GaAs substrate partially masked by reactively sputtered aluminum nitride (AlN). Epitaxial layers of GaAs were grown on unmasked GaAs by the pyrolysis of $Ga(CH_3)_3$ and arsine. GaAs deposited on AlN was a high-resistivity polycrystalline material. Polycrystalline GaAs deposition is undesirable for device fabrication, however, and it could be eliminated by a proper procedure. Tokumitsu *et al.*[26] observed no deposition of GaAs on a SiO_2 film in the $Ga(CH_3)_3$–As_4 system. Kamon *et al.*[40] studied selective growth of GaAs by low-pressure MOVPE at 10 Torr on a GaAs (001) substrate partially masked with a SiN_x film using $Ga(CH_3)_3$ and arsine (10% in H_2). A GaAs epitaxial layer was selectively grown on the unmasked area. Kamon *et al.*[41] achieved selective growth of $Al_xGa_{1-x}As$ ($0<x<0.35$) embedded in grooves by low-pressure MOVPE at 10 Torr using $Al(CH_3)_3$, $Ga(CH_3)_3$ and arsine (10 % in H_2). By precise control of the growth thickness, planar buried structures of GaAs and $Al_xGa_{1-x}As$ multilayers were obtained in grooves 3–1000 μm in width. No polycrystalline deposition occurred on areas masked with SiN_x films.

Nishizawa *et al.*[42] reported the success of GaAs atomic layer epitaxy (ALE) using $Ga(CH_3)_3$ and arsine. ALE is defined as a crystal-growth method using chemical reaction of adsorbates on the semiconductor surface, where gas molecules containing one of the semiconductor elements are introduced alternately into the growth chamber, by which process a single layer of film growth develops. Photo-ALE using either a high-pressure mercury lamp or an argon ion laser (or its frequency-doubled output) largely decreased the growth temperature and improved the surface morphology. Nishizawa *et al.*[43] studied the quality of GaAs epitaxial layers prepared by ALE with and without UV-light irradiation. Substrate temperatures of 500 °C for $Ga(CH_3)_3$ and arsine, and 300 °C for $Ga(C_2H_5)_3$ and arsine, fulfilled the conditions for monolayer growth. UV-light irradiation with an excimer laser improved the surface morphology and in certain instances also improved impurity concentrations. Ozeki *et al.*[44]

developed ALE of GaAs and AlAs using alternating pulses of $Ga(CH_3)_3$ or $Al(CH_3)_3$ and arsine, separated by purging hydrogen gas pulses. Nishizawa *et al.*[45] demonstrated ALE of GaAs in $Ga(CH_3)_3$– and $Ga(C_2H_5)_3$–arsine systems on various faces of GaAs substrate, and monomolecular layer growth was realized for the (100) face in the $Ga(CH_3)_3$–arsine system. From mass spectroscopic measurements and photoirradiation effects (by excimer lasers), the formation and migration of complex Ga adsorbates such as $Ga(CH_n)_x$ were supposed, in which $x=0$ at $T>520\,°C$ and $x=1$ at $T<500\,°C$.

Aoyagi *et al.*[46] observed an enhanced crystal growth of GaAs in MOCVD under laser illumination. They used $Ga(CH_3)_3$ and arsine, with an argon ion laser. The laser enhancement was attributed to photochemical processes such as photoassisted catalytic or surface effects. The laser enhancement made patterned crystal growth in MOCVD possible. Doi *et al.*[47,48] described stepwise monolayer epitaxy of GaAs using the switched laser MOVPE technique, using $Ga(CH_3)_3$ and arsine (20 % in H_2). By this method they were able to obtain the ideal growth rate of one monoatomic layer/cycle. Aoyagi *et al.*[49] reported the growth characteristics of laser MOVPE of GaAs using $Ga(CH_3)_3$ and arsine with an argon ion laser. The growth rate under laser MOVPE decreased with increasing substrate temperature, in contrast to the conventional MOVPE. Ohno *et al.*[50] realized ALE of GaAs with $Ga(C_2H_5)_3$ and arsine in a conventional atmospheric-pressure MOVPE reactor. The use of $Ga(C_2H_5)_3$ and arsine resulted in ALE growth of GaAs in rather limited ranges of substrate temperature and $Ga(C_2H_5)_3$ supply rate. Kawakyu *et al.*[51] reported complete self-limiting monolayer growth of GaAs ALE using $Ga(CH_3)_3$ and arsine, with a KrF excimer laser (248 nm). With laser irradiation, monolayer growth was achieved for a relatively wide temperature range from 470 °C to 530 °C. Without laser irradiation, ALE was possible for an extremely narrow temperature range around 500 °C. Mori *et al.*[52] reported the ALE growth of GaAs using diethylgallium chloride and arsine.

Kukimoto *et al.*[53] reported increase or decrease of carrier concentration in the selectively irradiated area of a GaAs epitaxial layer and the growth of an AlGaAs layer with higher aluminum content in the laser-irradiated area than in the unirradiated area, using laser (193 nm)-assisted MOVPE with $Ga(CH_3)_3$, $Al(CH_3)_3$ and arsine. Kusano *et al.*[54] reported laser irradiation effects on photoluminescence spectra of undoped GaAs which was grown by MOVPE using $Ga(CH_3)_3$ and arsine. The enhancement of the incorporation of the carbon acceptor and the increase of luminescence intensity were recognized as an argon ion laser irradiation effect. It was suggested that surface reactions between the radicals involving gallium atoms and photoinduced carriers at the substrate surface were enhanced by laser irradiation.

Epitaxial growth of GaAs layers on silicon substrates has been attempted to utilize the high electron mobility and direct band structure of GaAs in conjunction with the superior properties of silicon as a semiconductor with good crystallinity and mechanical hardness, etc. Usually germanium layers were used as the buffer layers to relax the lattice mismatch. However, Akiyama *et al.*[55] succeeded in the direct epitaxial growth of GaAs layers on silicon substrates without germanium buffer layers by MOCVD using $Ga(CH_3)_3$ and arsine in hydrogen carrier gas. The GaAs layers grown showed a high mobility of $5200\ cm^2\ V^{-1}\ s^{-1}$ at room temperature. Nonaka *et al.*[56] fabricated GaAs metal–semiconductor field-effect transistors (MESFETs) and ring oscillators on the GaAs layer on a silicon substrate. They used the MOCVD technique. Concerning high electron mobility transistors (HEMTs), leading to the possibility of large-scale production of high-speed digital integrated circuit (IC), Kobayashi *et al.*[28] obtained the high mobility of a two-dimensional electron gas, $\mu = 445\,000\ cm^2\ V^{-1}\ s^{-1}$, using MOCVD with $Ga(C_2H_5)_3$ and $Al(C_2H_5)_3$. Tanaka *et al.*[57] reported multi-wafer growth of HEMT large scale integration (LSI)-quality AlGaAs/GaAs selectively doped heterostructures by atmospheric pressure MOCVD using $Ga(CH_3)_3$, $Al(CH_3)_3$, arsine and disilane in hydrogen carrier gas. Kitahara *et al.*[58] reported the initial stages of GaAs and AlAs growth on silicon substrates, focusing on that performed by ALE using $Ga(CH_3)_3$, $Al(CH_3)_3$ and arsine. Their measurements showed that ALE on silicon substrates starts from three-dimensional growth but changes to layer-by-layer growth at an early stage.

The MOCVD or MOVPE techniques can be used for the fabrication of such layered devices as double heterostructure (DH) laser diodes, superlattices, and multiquantum well (MQW) heterostructures. Hino *et al.*[59] achieved room-temperature pulsed operation of AlGaInP DH diodes grown by MOCVD. Ikeda *et al.*[60] achieved

continuous-wave (CW) operation of an AlGaInP DH laser diode at 77 K grown by atmospheric MOCVD (600 °C) using $Al(C_2H_5)_3$, $Ga(C_2H_5)_3$, $In(C_2H_5)_3$ and phosphine. Hydrogen selenide (H_2Se) and $Zn(CH_3)_2$ were used as n-type and p-type dopants, respectively. Hino *et al.*[61] succeeded in CW (77 K) lasing operation with the yellow (583.6 nm) emitting AlGaInP DH laser diodes (on GaAs substrates) by low-pressure MOVPE using $Al(C_2H_5)_3$, $Ga(C_2H_5)_3$, $In(C_2H_5)_3$, phosphine and arsine. Magnesium from cyclopentadienylmagnesium (Cp_2Mg) was used as a p-type dopant. Hydrogen selenide was used as an n-type dopant source. Ikeda *et al.*[62] achieved CW operation at temperatures up to 33 °C with an AlGaInP/GaInP mesa stripe laser. The epitaxial layers were grown at 610 °C at atmospheric pressure by MOCVD using the triethyl metals and phosphine. Ishikawa *et al.*[63] achieved room-temperature CW operation for InGaP/InGaAlP DH laser diodes on GaAs substrates. The DH wafers were grown by low-pressure MOCVD using methyl metal–organics $In(CH_3)_3$, $Ga(CH_3)_3$, $Al(CH_3)_3$, phosphine and arsine. Hydrogen selenide and $Zn(CH_3)_2$ were used as dopant sources for the n- and p-type lasers, respectively.

GaInAsP/InP distributed-feedback buried heterostructure (DFB-BH) laser diodes which emit at 1.55 μm are important for optocommunication. Low threshold currents are strongly required for high reliability of the devices and their application to optoelectronic ICs. Yamada *et al.*[64] reported a DFB-BH laser with a threshold current of 9 mA entirely grown by MOVPE. Yoshida *et al.*[65] reported a 1.3 μm (CW) InGaAsP/InP DFB laser diode with a threshold current of 3.8 mA by a MOCVD/LPE (liquid phase epitaxy) hybrid process.

Tokumitsu *et al.*[66] prepared GaAs and $Ga_{1-x}Al_xAs$ multilayer structures by MOMBE growth using $Ga(C_2H_5)_3$ and $Al(C_2H_5)_3$. n-GaAs/p-GaAs multilayer structures were formed by applying an alternating ionization voltage to hydrogen. A single-crystal $Ga_{1-x}Al_xAs$ ternary alloy with good surface morphology was grown by introducing $Al(C_2H_5)_3$ as an aluminum source. A (GaAl)As/GaAs MQW heterostructure was also fabricated by switching $Al(C_2H_5)_3$. Ishibashi *et al.*[67] investigated the optical properties of $(AlAs)_n(GaAs)_n$ superlattices ($n = 1$–24) which were grown by MOCVD using $Ga(CH_3)_3$, $Al(CH_3)_3$ and arsine under atmospheric pressure at 750 °C. The superlattice samples obtained consisted of several tens to hundreds of periods of $(AlAs)_n(GaAs)_n$ alternating layers with total thickness of about 340 nm.

The band-gap energy of MOVPE-grown $Ga_{0.5}In_{0.5}P$ lattice matched to (001) GaAs can have various values for various Group V/III ratios in gas-phase composition and growth temperatures, as reported by Gomyo *et al.*[68] An interesting '50 meV problem' arose, namely the band-gap energy for MOVPE-grown $Ga_{0.5}In_{0.5}P$ was either 'normal' ~1.9 eV or 'abnormal' ~1.85 eV. Gomyo *et al.* later showed[69] evidence that these correspond to the random and ordered distribution of indium and gallium in the Group III sublattice. Complete ordering would have led to a $(GaP)_n(InP)_n$ superlattice.

Fukui[70] reported the growth and properties of epitaxial wafers composed of $(InAs)_1(GaAs)_1$ monolayer structures by low-pressure MOCVD using $Ga(C_2H_5)_3$ and $In(C_2H_5)_3$ as the Group III metal–alkyl sources, and arsine and phosphine as the Group V hydride sources. Solid composition in the $[(InAs)_1(GaAs)_1]_1$/InP heterojunction interface was also studied using the surface-sensitive extended X-ray absorption fine structure (EXAFS) technique. Kawaguchi and Asahi[71] has grown InGaAs/InP MQW structures on a (100) InP substrate by MOMBE using $In(C_2H_5)_3$ or $In(CH_3)_3$, $Ga(C_2H_5)_3$, arsine and phosphine. In order to prepare a nanometer-size semiconductor structure in the lateral direction, $(AlAs)_{0.5}$-$(GaAs)_{0.5}$ fractional-layer superlatices (FLS) with a new periodicity, perpendicular to the growth direction, were grown by Fukui *et al.*[72,73] using MOCVD on (001) GaAs substrates, slightly misoriented towards [$\bar{1}$10]. $Ga(C_2H_5)_3$ and $Al(C_2H_5)_3$ were used with arsine. In this technique the GaAs substrate was cut to expose a staircase-like structure with the level difference of a monoatomic layer (0.28 nm). In deposition, atoms arriving on a terrace are taken into the crystal from the atomic step side, and the deposition is made as the step moves outwards on the terrace surface (step–flow mode). AlAs is deposited to cover just half of the terrace surface, and then GaAs is deposited to cover another half. By repeating this procedure, the FLS was made. These growth techniques allow quantum well wires with dimensions < 10 nm to be frabricated without resorting to lithographic processes.

$InAs_{1-x}Sb_x$ ternary alloys are attractive materials for IR light sources, detectors and microwave applications, because of their small energy gaps and high electron mobilities. Fukui and

Horikoshi[74] performed MOVPE growth of $InAs_{1-x}Sb_x$ on an InAs substrate using $In(C_2H_5)_3$, $Sb(C_2H_5)_3$ and arsine. These authors[75] reported also MOVPE growth of InP using $In(C_2H_5)_3$ and phosphine on a semi-insulating InP substrate. They[76] reported the growth of an InAsSbP–InAs superlattice by MOVPE.

Thermodynamic analyses of solid versus vapor composition diagrams in MOVPE of Group III–V ternary or quarternary systems were made by Seki and Koukitu[77] and Koukitu *et al.*[78,79]

Group II–VI compound semiconductors

Group II–VI compound semiconductors have excellent prospects as optoelectronics materials, in view of the wide range of their band gaps (0–3.7 eV). Especially, ones with wide gaps (ZnS, ZnSe, CdS, ZnTe and their mixed crystals) are very useful as blue-emissive diodes and visible-light lasers for high-density memory. Concerning wide-gap Group II–VI compound semiconductors, Fujita *et al.*[80] examined the growth temperature dependence of crystallographic and luminescent properties of ZnSe, ZnS and ZnS_xSe_{1-x} epilayers grown by a low-pressure MOVPE using $Zn(CH_3)_2$ and hydrogen sulfide and hydrogen selenide (used as a 10 % or 5 % mixture in H_2). High-quality ZnSe and ZnS_xSe_{1-x} ($x = 0.02$–0.05) layers were obtained on GaAs substrates at a growth temperature of as low as 250 °C. They[81] studied the influence of reactor pressure (0.1–10 Torr) on the growth rate and electrical and luminescent properties.

GaAs, which is closely lattice-matched to ZnSe, has been used exclusively as a substrate material in epitaxial growth. However, this heteroepitaxial system of ZnSe/GaAs inherently involves 0.27 % of lattice mismatch. Fujita *et al.*[82] investigated the effects of lattice distortion due to the mismatch on crystallographic, electrical, and luminescence properties of ZnSe layers on GaAs substrates by examining the variation of these properties with layer thickness. The ZnSe layer was grown by low-pressure MOVPE using $Zn(CH_3)_2$ and hydrogen selenide (5 % in H_2). The epitaxial layer became free from the distortion at a position further than 2 μm away from the heterointerface. Hirabayashi and Kogure[83] found that zinc sulfide (ZnS) can be grown epitaxially on an Si (111) substrate by depositing a thin ZnS buffer layer on the substrate prior to the epitaxial growth. They used the MOCVD technique with $Zn(CH_3)_2$ and hydrogen sulfide (5 % in H_2).

Ando *et al.*[84] reported the growth of ZnSe thin films on (100) GaAs and glass substrates by photoenhanced MOCVD from $Zn(C_2H_5)_2$ and $Se(CH_3)_2$ (pure) with a low-pressure mercury lamp as a light source. The process temperature was 200–500 °C. Without UV irradiation, the growth rate decreased rapidly below 400 °C whereas, with irradiation, the growth occurred in the whole temperature range. Mino *et al.*[85] fabricated Al/ZnSe:Mn/ITO (indium tin oxide) dc-electroluminescent cells by plasma-assisted MOCVD. The organometallic sources were $Zn(C_2H_5)_2$, $Se(C_2H_5)_2$ and di-π-cyclopentadienylmanganese (Cp_2Mn).

Mitsuhashi *et al.*[86] studied the MOCVD of ZnSe on (100) GaAs substrates. They reported the dependence of growth rate on growth temperature (400–600 °C) and transport rate of source materials. The growth rate at higher temperatures (500–600 °C) was characterized by the mass transport of $Zn(C_2H_5)_2$, $Zn(CH_3)_2$, $Se(C_2H_5)_2$ and $Se(CH_3)_2$, whilst at lower temperatures (400–500 °C), the growth rate was limited by a kinetic process occurring on the growth surface. Yasuda *et al.*[87] prepared low-resistivity (3×10^{-2} Ω cm) aluminum-doped zinc sulfide layers by low-pressure MOVPE using a Lewis acid–base adduct of $Zn(C_2H_5)_2$–$S(C_2H_5)_2$ and hydrogen sulfide as source materials and $Al(C_2H_5)_2$ as an n-type dopant.

Oda *et al.*[88] proposed a new technique called hydrogen radical assisted MOCVD of ZnSe using $Zn(C_2H_5)_2$ (bubbled with hydrogen) as a zinc source and hydrogen selenide, SeF_6 or $Se(C_2H_5)_2$ (bubbled with hydrogen) as a selenium source. The chemical activity of hydrogen radicals was utilized in the growth of ZnSe on glass substrates. Hydrogen radicals (generated by a microwave discharge system) were used to improve the quality of films in various ways, e.g. in eliminating impurities by forming volatile hydrides or in passivating grain boundaries or pendant or dangling bonds.

Thin-film electroluminescent devices have been intensively studied because of their high potential to meet commercial demand for flat-type display panels. The MOCVD technique is advantageous in the inexpensive preparation of large-area thin films. Hirabayashi and Kozawaguchi[89] fabricated ac thin-film ZnS:Mn electroluminescent devices by MOCVD using $Zn(CH_3)_2$ and hydrogen sulfide as source gases and tricarbonyl-methyl-cyclopentadienylmanganese ($CH_3CpMn(CO)_3$) as dopant gas. The device gave electroluminescence

with a peak at 580 nm. Fujita *et al.*[90] prepared a ZnSe–$ZnS_{0.1}Se_{0.9}$ strained-layer superlattice (SLS) on a (100) GaAs substrate at a growth temperature of 400 °C by a low-pressure MOVPE using $Zn(CH_3)_2$, hydrogen selenide and hydrogen sulfide as sources. The average lattice parameter of the SLS was equal to that of GaAs. The SLS exhibited strong blue photoluminescence.

Photoassisted epitaxy of wide-gap Group II–VI compounds has attracted considerable attention, since the photoirradiation is effective for the enhancement of growth rate of the films and/or the growth of high-quality layers. Even fairly low-energy photons, such as visible light from a xenon lamp, were found to contribute to growth rate enhancement in MOVPE of ZnSe or ZnS using $Zn(CH_3)_2$, $Se(CH_3)_2$ or $Se(C_2H_5)_2$ (with hydrogen carrier gas), and $S(C_2H_5)_2$ or methylmercaptan (CH_3SH).[91–93] The irradiated wavelength dependence of the growth rate indicated that carriers generated at the growing surface promoted the surface reaction, because the longest wavelength for increased growth rate was 500 and 335–350 nm for ZnSe and ZnS respectively, nearly corresponding to the band-gaps of the epilayers at the growth temperature. Yoshikawa *et al.*[94] investigated the detailed features of photoassisted MOVPE of ZnSe layers [using $Zn(CH_3)_2$ and $Se(CH_3)_2$] by the use of an argon ion laser. It was reconfirmed that the absorption of photons by the ZnSe layer was essential for growth rate enhancement. The important role of hydrogen gas in the reaction between $Zn(CH_3)_2$ and $Se(CH_3)_2$ to form ZnSe under photoirradiation was found.

When p-type ZnS layers are combined with n-type layers, blue-light-emitting p–n junctions can be fabricated. With this goal in mind, Yasuda *et al.*[95] reported the MOVPE of p-type ZnSe using $Zn(CH_3)_2$ and $Se(C_2H_5)_2$ as source materials and lithium nitride (Li_3N) as the dopant. Mitsuishi *et al.*[96] reported the growth of p-type lithium-doped ZnS epitaxial layers on GaAs by MOVPE, using a $Zn(CH_3)_2$–$S(C_2H_5)_2$ adduct and hydrogen sulfide. The adduct was formed *in situ* by mixing vapors before introducing them into the reactor. Cyclopentadienyllithium (CpLi) was used as a dopant.

Metals

Deposition of a refractory metal thin film is especially important for applications to device processing, such as pinhole defect repairing in photolithographic masks. It is also important for direct writing of integrated circuits. Yokoyama *et al.*[97] reported laser-induced metal (molybdenum and chromium) deposition from organometallic solutions ($Mo(C_6H_6)_2$ and $Cr(C_6H_6)_2$ in benzene), using an argon ion laser at 488 nm. Yokoyama *et al.*[98] deposited a chromium film from $Cr(CO)_6$ under KrF excimer laser irradiation. Film quality was found to depend remarkably on laser intensity. A CW argon ion laser was used with its second harmonic to separate photochemical and photothermal effects. Photoinduced surface heating was found to be very important for obtaining a metallic film of good quality in this case. Yamagishi and Tarui[99] prepared a tantalum oxide film from $Ta(OCH_3)_5$ at low temperatures (150–400 °C) by photo-CVD using a low-pressure mercury lamp. Kasatani *et al.*[100] deposited copper and copper oxide (CuO) films from cupric acetate in ethanol and aqueous solutions, respectively, using an excimer laser (248 nm).

Aluminum is an important material for writing of integrated circuits. Hanabusa *et al.*[101] found dimethylaluminum hydride $(CH_3)_2AlH$ to be useful as a new source gas for photodeposition of aluminum films at a low carbon level when it was used with photons with wavelengths below 200 nm. Illumination was effective not only in producing films at a substrate temperature lower than required in thermal decomposition, but also in reducing the electrical resistivity of the deposited films.

Nambu *et al.*[102] used tungsten hexacarbonyl [$W(CO)_6$] in high-speed (300 $\mu m\ s^{-1}$) direct writing of tungsten conductors on a Si–LSI (large scale integration) substrate with low-pressure MOCVD. The limiting factor of the deposition rate was found to be the transport rate of the reactant into the reaction zone.

Suzuki *et al.*[103] reported spatially and time-resolved detection of gallium atoms formed in the excimer-laser photo-MOCVD of $Ga(CH_3)_3$ at 248 nm using the laser-induced fluorescence technique. The importance of chemically adsorbed species in the photo-MOCVD process was demonstrated.

Superconducting oxides

No words are necessary to express the strong enthusiasm concerning high-temperature superconducting materials. There have been several reports on their preparation using metal chelate compounds. Nakamori *et al.*,[104] Yamane *et al.*[105] and Oda *et al.*[106] prepared $YBa_2Cu_3O_x$ thin films

by chemical vapor deposition (CVD) using metal chelates (β-diketonates of barium, yttrium and copper) as source materials.

Other inorganic materials

Takahashi *et al.*[107] prepared a vanadium dioxide (VO_2) film by heating vanadyl tri(isobutoxide) [$VO(i\text{-}C_4H_9O)_3$] at 550–650 °C under a flow of oxygen. A V_2O_5 film was obtained above 650 °C. The VO_2 films are useful as temperature-sensing material, since VO_2 has a metal-to-semiconductor transition at 60–70 °C. Formation of ultrafine zirconia (ZrO_2) particles by the pyrolysis of zirconium tetra (t-butoxide) [$Zr(t\text{-}C_4H_9O)_4$] vapor was reported by Adachi *et al.*[108] Zirconia thus prepared has a thermally unstable tetragonal structure. Preparatin of InS and InS_2 from $(i\text{-}C_4H_9)_2In(S\text{—}i\text{-}C_3H_7)$ and $n\text{-}C_4H_9In(S\text{—}n\text{-}C_4H_9)_2$ was reported by Nomura *et al.*[109]

PART II: RESEARCH RELATED TO DIRECT USE OF ORGANOMETALLIC COMPOUNDS AND FUNDAMENTAL RESEARCH

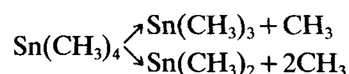
There is a variety of research activities concerning organometallic compounds related to their direct use in microelectronics in Japan. Reports on them are distributed among a vast volume of literature. Only three topics are addressed here as examples, namely spectroscopy and photochemistry, metal complexes and organometallic polymers. Again the coverage is very limited.

Spectroscopy and photochemistry of simple organometallic compoudś

Molecular electronic spectra of organometallic compounds are of key importance to photolytic dissociation reactions such as those in photo-MOCVD. As a matter of fact, such data are very scanty. There are a few contributions from Japanese investigators. Ito *et al.*[110] reported vacuum ultraviolet (VUV) absorption cross-sections of SiH_4, GeH_4, Si_2H_6 and Si_3H_8. Ibuki *et al.*[111] presented He(I) photoelectron spectra (PES) and photoabsorption cross-sections of $Ga(CH_3)_3$ and $In(CH_3)_3$ in the 106–270 nm range. The broad absorption bands observed for the trimethylmetals were attributed to *n*s-terminating Rydberg transitions of the outer orbital electrons. Ibuki *et al.*[112] also reported the photoabsorption cross-sections in the 106–270 nm range for $M(CH_3)_2$ (M = Zn, Cd and Hg).

Absorption spectra in the adsorbed states are very important in some photo-MOCVD processes in which the photolytic reaction occurs on the surface of solid substrates. Absorption bands of molecules usually shift to longer wavelength (red shift) on adsorption on solid substrates. Such data are, however, almost nonexistent except for a few cases. Sasaki *et al.*[113] gave a report on UV absorption spectra of adlayers of $Ga(CH_3)_3$ and arsine on silica substrates. Chemisorbed $Ga(CH_3)_3$ showed a spectrum quite different from that of vapor. Interestingly, arsine could be chemisorbed on the chemisorbed $Ga(CH_3)_3$ layer, although it could not be chemisorbed on silica. The spectrum of the co-chemisorbed layer of both components extended to a much longer wavelength. It is expected that absorption bands of $Ga(CH_3)_3$ adsorbed on arsenic in a GaAs substrate surface extends to longer wavelength than those of $Ga(CH_3)_3$ adsorbed on gallium. Irradiation with light of long wavelength can selectively decompose only $Ga(CH_3)_3$ on arsenic, leading to a self-limiting monoatomic layer control for gallium, essential for ALE.

Basic studies on photodissociation reactions of simple organometallic compounds in the gas phase attract a great deal of current attention. Kawasaki *et al.*[114] photodissociated tetramethyltin [$Sn(CH_3)_4$] at 193 nm. Methyl radicals obtained were probed by a time-of-flight (TOF) mass spectrometer and the reaction mechanisms were discussed. Two reaction channels, viz.



$$Sn(CH_3)_4 \begin{cases} \nearrow Sn(CH_3)_3 + CH_3 \\ \searrow Sn(CH_3)_2 + 2CH_3 \end{cases}$$

were proposed. Ueda *et al.*[115] used synchrotron orbit radiation (SOR) of 400–600 eV (38.6–57.9 MJ mol^{-1}) to excite tetramethyltin, resulting in core-level photoionization. Ionic fragments were detected by a TOF mass spectrometer. Production of small ionic fragments Sn^+, CH_m^+ ($m = 0\text{–}2$) and H^+ is strongly enhanced by tin 3*d* photoionization above 500 eV (48.2 MJ mol^{-1}). Nagaoka *et al.*[116] observed ionic fragmentation following inner-shell (lead 5*p* and 4*f*, carbon 1*s*) excitation of $Pb(CH_3)_4$ by use of SOR and TOF mass spectrometry. Inoue and Suzuki[117] observed laser-induced fluorescence of

the SiH_2 radical in the photolysis of phenylsilane by an ArF excimer laser. Shimo *et al.*[118] reported laser-ignited explosive decomposition of organometallic compounds (tetramethyl-lead, tetraethyl-lead and trimethylbismuth) using an excimer laser [ArF (193 nm) or KrF (248 nm)]. A single laser pulse triggered a thermal chain reaction and fine metal particles were obtained. Majima *et al.*[119] reported the SF_6-sensitized IR photodecomposition of $Fe(CO)_5$. Iron particles were obtained as final products besides CO. The iron particles were found to be γ-iron or austenite, including 0.75 wt % carbon, which has a mean particle size of 80 Å (8 nm) and a face-centered-cubic structure.

Metal complexes for microelectronic devices

Rare-earth metal–diphthalocyanine complexes are multicolored electrochromic materials. Yamamoto *et al.*[120] investigated electrochromism of an erbium–diphthalocyanine complex film with a glass/ITO/$ErH(Pc)_2$ + LiF/LiF + $CaCl_2$/Ag solid cell (ITO = indium tin oxide). The fast colour change from green to purple–red was observed when a positive voltage of about 2 V was applied to the ITO electrode. Kokado's group[121] prepared a solid electrochromic display (ECD) cell using evaporated thin films of lutetium–diphthalocyanine on ITO-coated glass. The solid electolyte was PbF_2. The ECD cell having a structure, ITO/$HLuPc_2$/PbF_2/Au quickly changed its colour from the original green to orange on application of a positive voltage of 1–2 V to the ITO electrode. The response time was less than 100 ms and the electrochromic reaction could be repeated well up to 10^5 times.

Langmuir–Blodgett (LB) films of metallophthalocyanines (MPcs) attract much attention because of their utility in photovoltaic cells and gas sensors. Nakahara *et al.*[122] studied reversible electrochromism for phthalocyanine (Pc) multilayers on ITO electrodes in an aqueous solution of KCl. Ogawa *et al.*[123] fabricated highly ordered monolayer assemblies of several metallophthalocyanine derivatives, e.g. copper tetrakis(n-butoxycarbonyl)phthalocyanine, as revealed by anisotropy in absorpton spectra. Fukui *et al.*[124] made a structural characterization of nickel phthalocyanine LB multilayer asemblies by FT-IR spectroscopy.

Sakaguchi *et al.*[125] prepared an alternating Y-type Langmuir–Blodgett multilayer capable of second harmonic generation (SHG), by the use of an amphiphilic ruthenium(II) tris(2,2′-bipyridine) complex. The second harmonic light intensity showed a large angular dependence. This finding, together with the electronic absorption spectra, indicated that the SHG was due to metal-to-ligand charge-transfer (MLCT) transition of the ruthenium complex.

Organometallic polymers for microelectronic devices

Ishikawa *et al.*[126] succeeded in 1984 in the synthesis of polymers in which silicon–silicon bonds and phenylene groups are contained alternately. Since then they have made a systematic study on organosilicon polymers in which a disilanylene group and a π-electronic system alternate, such as $(SiRMe—SiRMe—C_6H_4)_n$, R = Ph (**1**) or Et (**2**). The films of these polymers showed very high resistance to etching in an oxygen plasma, and so can be utilized as the top imaging layer in double-layer resists for lithographic applications. UV irradiation of the polymer films can convert them into compounds with low molecular weight. A resist pattern with a line width of 0.5 μm and an aspect ratio >3.0 can be obtained by UV irradiation of the film through a photomask, followed by treatment with oxygen plasma.[127] Moreover, highly conducting polymer films can be obtained by the treatment of **1** by antimony pentafluoride.[128]

Concerning conducting and semiconducting organometallic polymers, Yasuda *et al.*[129] synthesized poly[$Fe(CO)_3$(3-{(vinyloxy)ethyl}-η^4-1,3-pentadiene)] and poly[$Ru(CO)_3$(3-{(vinyloxy)ethyl}-η^4-1,3-pentadiene)]. Both are electron conductors after doping with iodine. The conductivity was 3.2×10^{-3} S cm^{-1}, one of the highest values at that time for organometallic polymers. They prepared other types of semiconducting (on doping with iodine) polymers containing the $Fe(CO)_3X$ unit, where X = chlorine or bromine. Nogami *et al.*[130] found a doping effect for poly(methylene ditelluride), $(CH_2Te_2)_n$, and related polymers, $(CH_2Te)_n$, $(CH_2Se)_n$, $(p\text{-}CH_2C_6H_4CH_2Te)_n$ and $(p\text{-}CH_2C_6H_4CH_2Te_2)_n$. These polymers were found to give conductive materials (10^{-2}–10^{-7} S cm^{-1}) upon doping with bromine or iodine. Shirai *et al.*[131] obtained highly conducting (10^{-4}–10^{1} Ω^{-1} cm^{-1}) material by doping of films formed by covalently binding metal-2,9,16,23-tetracarboxyphthalocyanines to poly(2-vinylpyridine-*co*-styrene).

Organometallic polymers can be utilized as liquid-crystal materials. Takahashi *et al.*[132] reported that $(Pd(PBu_3)_2—C≡C—C≡C—Pt(PBu_3)_2—C≡C—C≡C)_n$ and $(Pd(PBu_3)_2—C≡C—C≡C—Pt(PBu_3)_2—C≡C—C_6H_4—C≡C)_n$ form lyotropic liquid crystals; they are nematic, the former being aligned perpendicular to the magnetic field, and the latter parallel to it.

Plasma polymerization of metallophthalocyanines was reported by Osada *et al.*[133–135] Fabrication of thin films (60–300 nm thick) was performed by evaporating the solid metallophthalocyanine by glow-discharge plasma polymerization. In the thin films obtained, the original structure of the metallophthalocyanine was largely maintained though phthalocyonine units were extensively cross-linked. The aluminum/polymeric CuPc/ITO sandwich cells were found to exhibit good rectification, photovoltaic, photoreduction and electrochromic characteristics.

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REFERENCES

1. Sato, H *Appl. Organomet. Chem.*, 1989, 3: 363
2. Hanabusa, M *Materials Sci. Repts*, 1987, 2: 51
3. Ghandhi, S K and Bhat, I B *MRS Bull.*, 1988 (Nov.): 37
4. Williams, J O *Angew. Chem. Int. Ed. Engl., Adv. Mater.*, 1989, 28: 1110
5. Manasevit, H M *Appl. Phys. Lett.*, 1968, 12: 156
6. Manasevit, H M and Simpson, W I *J. Electrochem. Soc.*, 1969, 116: 1725
7. Dupuis, R D and Dapkus, P D *Appl. Phys. Lett.*, 1977, 31: 466
8. Dupuis, R D and Dapkus, P D *IEEE J. Quantum Electron.*, 1978, QE-15: 128
9. Coleman, J J, Dapkus, P D, Thompson, D E and Clarke, D R *J. Cryst. Growth*, 1981, 55: 207
10. Dupuis, R D *Appl. Phys. Lett.*, 1979, 35: 311
11. Suntola, T and Antson, M US Patent 4 058 430 (1977)
12. Veuhoff, E, Pletschen, W, Balk, P and Luth, H *J. Cryst. Growth*, 1981, 55: 30
13. Kumagawa, M, Sunami, H, Terasaki, T and Nishizawa, J *Jpn. J. Appl. Phys.*, 1968, 7: 1332
14. Hanabusa, M, Namiki, A and Yoshihara, K *Appl. Phys. Lett.*, 1979, 35: 626
15. Mishima, Y, Hirose, M, Osaka, Y, Nagamine, K, Ashida, Y, Kitagawa, N and Isogaya, K *Jpn. J. Appl. Phys.*, 1983, 22: L46
16. Hanabusa, M, Moriyama, S and Kikuchi, H *Thin Solid Films*, 1983, 107: 227
17. Urisu, T and Kyuragi, H *J. Vac. Sci. Technol.*, 1987, B5: 1436
18. Kizaki, Y, Kandori, T and Fujitani, Y *Jpn. J. Appl. Phys.*, 1985, 24: 800
19. Kawasaki, M, Tsukiyama, Y and Hada, H *J. Appl. Phys.*, 1988, 64: 3254
20. Kawasaki, M, Hayashi, K and Hada, H *Oyo Butsuri*, 1986, 55: 606
21. Saitoh, T and Minagawa, S *J. Electrochem.*, 1973, 120: 656
22. Ito, S, Shinohara, T and Seki, Y *J. Electrochem. Soc.*, 1973, 120: 1419
23. Nakanisi, T, Udagawa, T, Tanaka, A and Kamei, K *J. Cryst. Growth*, 1981, 55: 255
24. Takagishi, S and Mori, H *Jpn. J. Appl. Phys.*, 1983, 22: L795
25. Takagishi, S and Mori, H *Jpn. J. Appl. Phys.*, 1984, 23: L100
26. Tokumitsu, E, Kudou, Y, Konagai, M and Takahashi, K *J. Appl. Phys.*, 1984, 55: 3163
27. Hata, M, Fukuhara, N, Zempo, Y, Isemura, M, Yako, T and Maeda, T *J. Cryst. Growth*, 1988, 93: 543
28. Kobayashi, N and Fukui, T *Electron. Lett.*, 1984, 20: 887
29. Seki, Y, Tanno, K, Iida, K and Ichiki, E *J. Electrochem. Soc.*, 1975, 122: 1108
30. Tokumitsu, E, Kudou, Y, Konagai, M and Takahashi, K *Jpn. J. Appl. Phys.*, 1985, 24: 1189
31. Kondo, K, Ishikawa, H, Sasa, S, Sugiyama, Y and Hiyamizu, S *Jpn. J. Appl. Phys.*, 1986, 25: L52
32. Ishikawa, H, Kondo, K, Sasa, S, Tanaka, H and Hiyamizu, S *J. Cryst. Growth*, 1986, 76: 521
33. Terao, H and Sunakawa, H *J. Cryst. Growth*, 1984, 68: 157
34. Fujita, S, Uemoto, Y, Araki, S, Imaizumi, M, Takeda, Y and Sasaki, A *Jpn. J. Appl. Phys.*, 1988, 27: 1151
35. Nishizawa, J and Kurabayashi, T *J. Electrochem. Soc.*, 1983, 130: 413
36. Yoshida, M, Watanabe, H and Uesugi, F *J. Electrochem. Soc.*, 1985, 132: 677
37. Mashita, M, Horiguchi, S, Shimazu, M, Kamon, K, Mihara, M and Ishii, M *J. Cryst. Growth*, 1986, 77: 194
38. Tsuda, M, Oikawa, S, Morishita, M and Mashita, M *Jpn. J. Appl. Phys.*, 1987, 26: L564
39. Nakai, K and Ozeki, M *J. Cryst. Growth*, 1984, 68: 200
40. Kamon, K, Takagishi, S and Mori, H *J. Cryst. Growth*, 1985, 73: 73
41. Kamon, K, Shimazu, M, Kimura, K, Mihara, M and Ishii, M *J. Cryst. Growth*, 1986, 77: 297
42. Nishizawa, J, Abe, H and Kurabayashi, T *J. Electrochem. Soc.*, 1985, 132: 1197
43. Nishizawa, J, Abe, H, Kurabayashi, T and Sakurai, N *J. Vac. Sci. Technol.*, 1986, A4: 706
44. Ozeki, M, Mochizuki, K, Ohtsuka, N and Kodama, K *J. Vac. Sci. Technol.*, 1987, B5: 1184
45. Nishizawa, J, Kurabayashi, T, Abe H and Sakurai, N *J. Vac. Sci. Technol.*, 1987, A5: 1572

46. Aoyagi, Y, Masuda, S, Namba, S and Doi, A *Appl. Phys. Lett.*, 1985, 47: 95
47. Doi, A, Aoyagi, Y and Namba, S *Appl. Phys. Lett.*, 1986, 48: 1787
48. Doi, A, Aoyagi, Y and Namba, S *Appl. Phys. Lett.*, 1986, 49: 785
49. Aoyagi, Y, Kanazawa, M, Doi, A, Iwai, S and Namba, S *J. Appl. Phys.*, 1986, 60: 3131
50. Ohno, H, Ohtsuka, S, Ishii, H, Matsubara, Y and Hasegawa, H *Appl. Phys. Lett.*, 1989, 54: 2000
51. Kawakyu, Y, Ishikawa, H, Sakaki, M and Mashita, M *Jpn. J. Appl. Phys.*, 1989, 28: L1439
52. Mori, K, Yoshida, M, Usui, A and Terao, H *Appl. Phys. Lett.*, 1988, 52: 27
53. Kukimoto, H, Ban, Y, Komatsu, H, Takeuchi, M and Ishizaki, M *J. Cryst. Growth*, 1986, 77: 223
54. Kusano, J, Segawa, Y, Iwai, S, Aoyagi, Y and Namba, S *Appl. Phys. Lett.*, 1988, 52: 67
55. Akiyama, M, Kawarada, Y and Kaminishi, K *Jpn. J. Appl. Phys.*, 1984, 23: L843
56. Nonaka, T, Akiyama, M, Kawarada, Y and Kaminishi, K *Jpn. J. Appl. Phys.*, 1984, 23: L919
57. Tanaka, H, Itoh, H, O'hori, T, Takikawa, M, Kasai, K, Takechi, M, Suzuki, M and Komeno, J *Jpn. J. Appl. Phys.*, 1987, 26: L1456
58. Kitahara, K, Ohtsuka, N and Ozeki, M *J. Vac. Sci. Technol.*, 1989, B7: 700
59. Hino, I, Gomyo, A, Kobayashi, K, Suzuki, T and Nishida, K *Appl. Phys. Lett.*, 1983, 43: 987
60. Ikeda, M, Mori, Y, Takiguchi, M, Kaneko, K and Watanabe, N *Appl. Phys. Lett.*, 1984, 45: 661
61. Hino, I, Kawata, S, Gomyo, A, Kobayashi, K and Suzuki, T *Appl. Phys. Lett.*, 1986, 48: 557
62. Ikeda, M, Nakano, K, Mori, Y, Kaneko, K and Watanabe, N *Appl. Phys. Lett.*, 1986, 48: 89
63. Ishikawa, M, Ohba, Y, Sugawara, H, Yamamoto, M and Nakanisi, T *Appl. Phys. Lett.*, 1986, 48: 207
64. Yamada, H, Sasaki, T, Takano, S, Numai, T, Kitamura, M and Mito, I *Electron Lett.*, 1988, 24: 147
65. Yoshida, N, Kimura, T, Mizuguchi, K, Ohkura, Y, Murotani, T and Kawagishi, A *J. Cryst. Growth*, 1988, 93: 832
66. Tokumitsu, E, Katoh, T, Kimura, R, Konagai, M and Takahashi, K *Jpn. J. Appl. Phys.*, 1986, 25: 1211
67. Ishibashi, A, Mori, Y, Itabashi, M and Watanabe, N *J. Appl. Phys.*, 1985, 58: 2691
68. Gomyo, A, Kobayashi, K, Kawata, S, Hino, I, Suzuki, T and Yuasa, T *J. Cryst. Growth*, 1986, 77: 367
69. Gomyo, A, Suzuki, T, Kobayashi, K, Kawata, S, Hino, I and Yuasa, T *Appl. Phys. Lett.*, 1987, 50: 673
70. Fukui, T *J. Cryst. Growth*, 1988, 93: 301
71. Kawaguchi, Y and Asahi, H *Appl. Phys. Lett.*, 1987, 50: 1243
72. Fukui, T, Saito, H and Tokura, Y *Jpn. J. Appl. Phys.*, 1988, 27: L1320
73. Fukui, T, Saito, H and Tokura, Y *Appl. Phys. Lett.*, 1989, 55: 1958
74. Fukui, T and Horikoshi, Y *Jpn. J. Appl. Phys.*, 1980, 19: L53
75. Fukui, T and Horikoshi, Y *Jpn. J. Appl. Phys.*, 1980, 19: L395
76. Fukui, T and Horikoshi, Y *Jpn. J. Appl. Phys.*, 1980, 19: L551
77. Seki, H and Koukitu, A *J. Cryst. Growth*, 1986, 74: 172
78. Koukitu, A, Suzuki, T and Seki, H *J. Cryst. Growth*, 1986, 74: 181
79. Koukitu, A and Seki, H *J. Cryst. Growth*, 1986, 76: 233
80. Fujita, S, Matsuda Y and Sasaki, A *J. Cryst. Growth*, 1984, 68: 231
81. Fujita, S, Yodo, T, Matsuda, Y and Sasaki, A *J. Cryst. Growth*, 1985, 71: 169
82. Fujita, S, Yodo, T and Sasaki, A *J. Cryst. Growth*, 1985, 72: 27
83. Hirabayashi, K and Kogure, O *Jpn. J. Appl. Phys.*, 1985, 24: 1590
84. Ando, H, Inuzuka, H, Konagai, M and Takahashi, K *J. Appl. Phys.*, 1985, 58: 802
85. Mino, N, Kobayashi, M, Konagai, M and Takahashi, K *Jpn. J. Appl. Phys.*, 1985, 24: L383
86. Mitsuhashi, H, Mitsuishi, I and Kukimoto, H *J. Cryst. Growth*, 1986, 77: 219
87. Yasuda, T, Hara, K and Kukimoto, H *J. Cryst. Growth*, 1986, 77: 985
88. Oda, S, Kawase, R, Sato, T, Shimizu, I and Kokado, H *Appl. Phys. Lett.*, 1986, 48: 33
89. Hirabayashi, K and Kozawaguchi, H *Jpn. J. Appl. Phys.*, 1986, 25: 711
90. Fujita, S, Matsuda, Y and Sasaki, A *Appl. Phys. Lett.*, 1985, 47: 955
91. Fujita, S, Tanabe, A, Sakamoto, T, Isemura, M and Fujita, S *Jpn. J. Appl. Phys.*, 1987, 26: L2000
92. Fujita, S, Tanabe, A, Sakamoto, T, Isemura, M and Fujita, S *J. Cryst. Growth*, 1988, 93: 259
93. Fujita, S, Takeuchi, F Y and Fujita, S, *Jpn. J. Appl. Phys.*, 1988, 27: L2019
94. Yoshikawa, A, Okamoto, T, Fujimoto, T, Onoue, K, Yamaga, S and Kasai H *Jpn. J. Appl. Phys.*, 1990, 29: L225
95. Yasuda, T, Mitsuishi, I and Kukimoto, H *Appl. Phys. Lett.*, 1987, 52: 57
96. Mitsuishi, I, Shibatani, J, Kao M-H, Yamamoto, M, Yoshino, J and Kukimoto, H *Jpn. J. Appl. Phys.*, 1990, 29: L733
97. Yokoyama, H, Kishida, S and Washio, K *Appl. Phys. Lett.*, 1984, 44: 755
98. Yokoyama, H, Uesugi, F, Kishida, S and Washio, K *Appl. Phys.*, 1985, A37: 25
99. Yamagishi, K and Tarui, Y *Jpn. J. Appl. Phys.*, 1986, 25: L306
100. Kasatani, K, Shinohara, H and Sato, H *Denki Kagaku*, 1989, 57: 1204
101. Hanabusa, M, Oikawa, A and Cai, P Y *J. Appl. Phys.*, 1989, 66: 3268
102. Nambu, Y, Morishige, Y and Kishida, S *Appl. Phys. Lett.*, 1990, 56: 2581
103. Suzuki, H, Mori, K, Kawasaki, M and Sato, H *J. Appl. Phys.*, 1988, 64: 371

104. Nakamori, T, Abe, H, Kanamori, T and Shibata, S *Jpn. J. Appl. Phys.*, 1988, 27: L1265
105. Yamane, H, Kurosawa, H, Iwasaki, H, Masumoto, H, Hirai, T, Kobayashi, N and Muto, Y *Jpn. J. Appl. Phys.*, 1988, 27: L1275.
106. Oda, S, Zama, H, Ohtsuka, T, Sugiyama, K and Hattori, T *Jpn. J. Appl. Phys.*, 1989, 28: L427
107. Takahashi, Y, Kanamori, M, Hashimoto, H, Moritani, Y and Masuda, Y *J. Mater. Sci.*, 1989, 24: 192
108. Adachi, M, Okuyama, K, Moon, S, Tohge, N and Kousaka, Y *J. Mater. Sci.*, 1989, 24: 2275
109. Nomura, R, Inagawa, S, Kanaya, K and Matsuda, H *Appl. Organomet. Chem.*, 1989, 3: 195
110. Itoh, U, Toyoshima, Y, Onuki, H, Washida, N and Ibuki, T *J. Chem. Phys.*, 1986, 85: 4867
111. Ibuki, T, Hiraya, A, Shobatake, K, Matsumi, Y and Kawasaki, M *Chem. Phys. Lett.*, 1989, 160: 152
112. Ibuki, T, Hiraya, A and Shobatake, K *J. Chem. Phys.*, 1990, 92: 2797
113. Sasaki, M, Kawakyu, Y and Mashita, M *Jpn. J. Appl. Phys.*, 1989, 28: L131
114. Kawasaki, M, Sato, H, Shinohara, H and Nishi, N *Laser Chem.*, 1987, 7: 109
115. Ueda, K, Shigemasa, E, Sato, Y, Nagaoka, S, Koyano, I, Yagishita, A, Nagata, T and Hayaishi, T *Chem. Phys. Lett.*, 1989, 154: 357
116. Nagaoka, S, Koyano, I, Ueda, K, Shigemasa, E, Sato, Y, Yagishita, A, Nagata, T and Hayaishi, T *Chem. Phys. Lett.*, 1989, 154: 363
117. Inoue, G and Suzuki, M *Chem. Phys. Lett.*, 1984, 105: 641
118. Shimo, T, Nakashima, N and Yoshihara, K *Chem. Phys. Lett.*, 1989, 156: 31
119. Majima, T, Ishii, T, Matsumoto, Y and Takami, M *J. Am. Chem. Soc.*, 1989, 111: 2417
120. Yamamoto, H, Noguchi, M and Tanaka, M *Jpn. J. Appl. Phys.*, 1984, 23: L221
121. Egashira, N and Kokado, H *Jpn. J. Appl. Phys.*, 1986, 25: L462
122. Nakahara, H, Fukuda, K, Kitahara, K and Nishi, H *Thin Solid Films*, 1989, 178: 361
123. Ogawa, K, Kinoshita, S, Yonehara, H, Nakahara, H and Fukuda, K *J. Chem. Soc., Chem. Commun.*, 1989: 477
124. Fukui, M, Katayama, N, Ozaki, Y, Araki, T and Iriyama, K *Chem. Phys. Lett.*, 1991, 177: 247
125. Sakaguchi, H, Nakamura, H, Nagamura, T, Ogawa, T and Matsuo, T *Chem. Lett.*, 1989: 1715
126. Ishikawa, M, Ni, H, Matsusaki, K, Nate, K, Inoue, T and Yokono, H *J. Polym. Sci., Polym. Lett. Ed.*, 1984, 22: 669
127. Nate, K, Inoue, T, Sugiyama, H and Ishikawa, M *J. Appl. Polym. Sci.*, 1987, 34: 2445
128. Ohshita, J, Furumori, K, Ishikawa, M and Yamanaka, T *Organometallics*, 1989, 8: 2084
129. Yasuda, H, Noda, I, Miyanaga, S and Nakamura, A *Macromolecules*, 1984, 17: 2453
130. Nogami, T, Tasaka, Y, Inoue, K and Mikawa, H *J. Chem. Soc., Chem. Commun.*, 1985, 269
131. Shirai, H, Higaki, S, Hanabusa, K, Hojo, N and Hirabaru, O *J. Chem. Soc., Chem. Commun.*, 1983, 751
132. Takahashi, S, Takai, Y, Morimoto, H and Sonogashira, K *J. Chem. Soc., Chem. Commun.*, 1984, 3
133. Osada, Y and Mizumoto, A *J. Appl. Phys.*, 1986, 9: 1776
134. Osada, Y, Mizumoto, A and Tsuruta, H *J. Macromol. Sci., Chem.*, 1987, A24: 403
135. Osada, Y, Mizumoto, A, Tsuruta, H, Shigehara, A and Yamada, A *Nippon Kagaku Kaishi*, 1987: 2019