Surface Processing and Laser Assisted Chemistry

SURFACE PROCESSING
AND
LASER ASSISTED CHEMISTRY

PROCEEDINGS OF SYMPOSIUM E ON
SURFACE PROCESSING AND LASER ASSISTED CHEMISTRY
OF THE 1990 E-MRS SPRING CONFERENCE

STRASBOURG, FRANCE, 29 MAY – 1 JUNE 1990

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1990
NORTH-HOLLAND
AMSTERDAM · NEW YORK · OXFORD · TOKYO

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This book is printed on acid-free paper.

ISBN: 0 444 88947 7

Published by:

North-Holland
Elsevier Science Publishers B.V.
P.O. Box 211
1000 AE Amsterdam
The Netherlands

Sole distributors for the USA and Canada:

Elsevier Science Publishing Company, Inc.
655 Avenue of the Americas
New York, NY 10010
USA

Reprinted from:
APPLIED SURFACE SCIENCE 46

The manuscripts for the Proceedings were received by the Publisher: July–August 1990

Library of Congress Cataloging-in-Publication Data

Printed in The Netherlands

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Preface

The Spring Conference of the European Materials Research Society (E-MRS) held in Strasbourg (France) every year, was again in 1990 one of the highlights in the field of Materials Research. In the following, the refereed papers of the Symposium "Surface Processing and Laser Assisted Chemistry" will give the reader a detailed overview of the progress achieved during the last year.

Invited speakers from Europe, Japan and the United States of America introduced the sessions covering all aspects of laser assisted surface processing ranging from the generation of high-T_c superconductor layer structures (T. Venkatesan of Bellcore, USA and F. Schmaderer of ABB, Germany) to industrial laser applications for device fabrication (F. Bachmann of Siemens, Germany and T. Bernhardt of Lawrence Livermore Lab, USA).

The E-MRS Conference in Strasbourg demonstrated again, that it is an efficient forum for interaction between basic research institutions and industry. The topics presented gave recent results in organometallic chemistry and laser photochemistry (D. Bradley, FRS of Queen Mary College London, UK and R. Larciprete of ENEA Frascati, Italy) and novel surface characterisation techniques (E. van Loenen of Philips Eindhoven, The Netherlands and J. Heidberg of Hannover University, Germany).

The ability to control the surface morphology by digital deposition and etching (Y. Horiike of Hiroshima University, Japan) shows one of the future directions for exciting applications of laser surface processing, some of which may apply UV and VUV excitation (S. Lazare of Bordeaux University, France and Y. Nissim of CNET, France).

The understanding of elementary processes is essential for the design of novel deposition methods, with diamond CVD being an outstanding example (J. Butler of Naval Research Lab, USA). The strong and increasing participation from leading companies around the world (ABB, Bellcore, Doduco, IBM, NEC, Philips, Siemens) once again showed, that E-MRS and its Spring and Fall Meetings every year brings together the leading scientists and engineers from all over the world into the stimulating atmosphere of Strasbourg and its Alsacian surroundings.

Merci, au revoir en 1991!

Ian W. Boyd
London

Eric Fogarassy
Strasbourg

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This conference was held under the auspices of:

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It is our pleasure to acknowledge with gratitude the financial assistance provided by:

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Applied Surface Science 46 (1990) 1–4
North-Holland

New metallo-organic precursors for surface processing

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Received 14 June 1990; accepted for publication 24 July 1990

Metallo-organic compounds have been used for the deposition, by thermolysis or photolysis, of a wide range of inorganic materials as films on a variety of surfaces. This paper reviews recent work on metallo-organic precursors for the deposition of films of metals, metal oxides, metal nitrides, metal fluorides and compound semiconductors.

1. Introduction

Since this article is concerned primarily with recent developments it will not deal with the historical development of the use of metallo-organic compounds as precursors for depositing films of materials. Suffice it to say that the requirements of the electronics industry have provided a major stimulus in the past ten years although other applications such as anti-reflective coatings on glass, anti-static coating and electrically conducting coatings have also played a significant part. Volatile precursors (e.g. compounds with vapour pressures of a few Torr at room temperature) may be deposited by MOCVD using a suitable carrier gas whereas less volatile precursors require the low-pressure regime ($\sim 10^{-3}$ Torr) without a carrier gas sometimes referred to as MOMBE. The ideal precursor must be stable enough at temperatures up to about 100 °C in order to generate sufficient vapour pressure but to be unstable at higher temperatures in order to give a facile decomposition on a heated substrate. In some applications it is desirable to photolyse the metallo-organic precursor and this gives an additional requirement which the chemist has to consider in the molecular design of precursors.

2. Metal films

There has been considerable activity in designing suitable precursors for the deposition of platinum, gold, copper and aluminium in recent years.

Puddephat and co-workers [1] showed that volatile organoplatinum(II) complexes such as cis-$[PtMe_2(MeNC)_2]$ (where Me = methyl and MeNC = methyl isonitrile) and $[PtMe_2(COD)]$ (where COD = 1,5-cyclo-octadiene) could be used to deposit platinum on a silicon substrate at 250 °C. Moreover, they showed that in the presence of hydrogen the carbon content of the platinum was considerably reduced and the deposition temperature could be lowered to 135–180 °C.

Using the platinum(IV) complex $[Pt(C_5H_5)Me_3]$ (where C_5H_5 = π-cyclopentadienyl) Koplitz et al. [2] were able to deposit platinum by laser-induced photolysis at room temperature and atmosphere pressure (argon).

Similarly gold has been deposited using $[AuMe(PMe_3)]$ and $[AuMe_3(PMe_3)]$ at low pressure at 200 °C [3] or by photothermal laser-induced deposition of $[AuMe_2(hfa)]$ (where hfa = hexafluoroacetylacetonate) [4].

Recent work has shown that $[Cu(C_5H_5)(PEt_3)]$ is a suitably volatile precursor for photothermal or

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laser-induced deposition of copper [5]. The copper(II) chelate complex $[Cu(OCHMeCH_2NMe_2)_2]$ has also been used for depositing metallic copper [6].

Various organoaluminium compounds such as $AlBu^i_3$ and $AlHBu^i_2$ (where Bu^i = isobutyl) have been used for depositing metallic aluminium for several years but carbon contamination has been a disadvantage. Considerable interest has recently been shown in the aluminium hydride complex $[AlH_3(NMe_3)_2]$ as a volatile precursor for aluminium deposition because it has no Al–C bonds and the trimethylamine molecule (NMe_3) is very stable thermally [7].

3. Metal oxide films

It has been known for many years that metal alkoxides $[M(OR)_x]_n$ are suitable precursors for the deposition of metal oxide films and this field has recently been reviewed [8]. The deposition of binary oxides such as Al_2O_3, TiO_2, ZrO_2, Ta_2O_5, etc., presents no problem since suitable volatile metal alkoxides are available commercially. However, some very interesting materials involve heterometal oxides such as $BaTiO_3$, $LiNbO_3$, $KTaO_3$, $Pb_{1-x}La_xTi_yZr_2O_3$ and $YBa_2Cu_3O_{7-x}$, and these present considerable problems for the MOCVD technique because of the disparity in volatility of the individual metal alkoxides which would be required as precursors. As alternatives to metal alkoxides some metal diketonates have been used especially for univalent and bivalent metals. Volatility is usually enhanced by using fluorinated ligands (e.g. hfa) but this may lead to the deposition of metal fluorides instead of oxides (see section 5).

4. Metal nitride films

Some metal nitrides are of considerable importance to the electronics industry. Thus aluminium nitride is an insulating material having a high thermal conductivity, gallium nitride is a semiconductor and titanium nitride is a metallic conductor which has advantages over gold or platinum under some circumstances.

New metallo-organic precursors for AlN film deposition have recently been reported. For example, the azide complex $[AlEt_2(N_3)]$ [9] and the amide complex $[AlMe_2(NH_2)]_3$ [10] have both been used successfully. The gallium azide $[GaEt_2(N_3)]$ has also been proposed as a precursor for the deposition of GaN [11]. Bradley and Thomas [12] synthesized a number of volatile transition-metal dialkylamides $[M(NR_2)_x]$ containing metal–nitrogen covalent bonds over thirty years ago but only recently have they been considered as precursors for metal nitride deposition.

Earlier work using $Ti(NMe_2)_4$ as precursor for TiN gave a material that was impure due to carbon incorporation [13] but recent work has shown that high-quality films containing less than 1 at% carbon can be deposited at 200 °C using $Ti(NMe_2)_4$ in conjunction with ammonia gas [14]. The azide complex $[Ti(C_5H_5)_2(N_3)_2]$ has also been used as a precursor for TiN [15].

5. Metal fluoride films

As mentioned earlier (section 3) the use of fluorinated diketones produces moderately volatile derivatives of bivalent metals and we have recently shown that the anhydrous calcium complex $[Ca(hfa)_2]$ is a suitable precursor for the photo-assisted deposition of CaF_2 on GaAs substrate at 100 °C [16]. The use of hfa complexes as precursors for depositing metal fluoride glasses has been patented [17].

6. Compound semiconductors

Perhaps the most stringent requirement for metallo-organic precursors has occurred in the field of III–V and II–VI compound semiconductors where extremely high purity is essential. Tremendous advances have been made during the past ten years but the field has recently been reviewed [18] and this article will mention only a few recent developments. A new class of non-pyrophoric organometallic precursors for aluminium,

gallium and indium has been developed using substituted alkyl groups which provide tertiary nitrogen donor atoms which bring about intramolecular coordination to the Group III metal by chelation [19]. Thus InP was grown epitaxially at 580–660 °C using (3-dimethylaminopropyl) dimethyl indium $[InMe_2(CH_2CH_2CH_2NMe_2)]$ with phosphine. This idea was developed further by using chelating alkyl groups [20]. For example, it was reported that AlGaAs could be deposited epitaxially using 1-(3-dimethylaminopropyl)-1-ala-cyclohexane $[Al(CH_2CH_2CH_2CH_2CH_2)(CH_2CH_2CH_2NMe_2)]$ and 1-(3-dimethylaminopropyl)-1-galla-cyclohexane $[Ga(CH_2)_5(CH_2CH_2CH_2NMe_2)]$ as the Group III precursors. An alternative approach using covalently bonded Group III – Group V compounds as single source precursors was first reported by Constant and co-workers [21] in the form of the trimeric compound $[GaEt_2PEt_2]_3$. Recent work has shown that $[InMe_2PBu^t_2]_2$ is suitable for the deposition of InP at low temperature under MOMBE conditions [22] and $[GaMe_2AsBu^t_2]_2$ may be used for the deposition of GaAs [23]. This interesting field has recently been reviewed by Cowley and Jones [24]. The low volatility of these single source precursors is a consequence of their dimeric or trimeric nature and it was expected that more volatile species would be obtained by using bulky alkyl groups on the Group III metal and generating a monomeric compound. Higa and George [25] have now reported the synthesis of monomeric $[GaBu^t_2AsBu^t_2]$ and its decomposition to GaAs at ~ 400 °C, whilst Cowley et al. [26] have synthesized the novel precursors $[InBu^t_2SbBu^t_2]$ and $[GaBu^t_2SbBu^t_2]$.

Another aspect of the compound semiconductor field has been the search for alternative precursors to the hydrides of Group V and Group VI elements. Thus Bu^tPH_2 and Bu^iPH_2 have been used as alternatives to PH_3 [27] and recently $C_6H_5AsH_2$ has been used as an alternative to AsH_3 [28]. Recent work on alternative Group VI precursors has led to the use of heterocyclic species such as thiophene (C_4H_4S) and selenophene (C_4H_4Se) [29] and di-isopropyl telluride ($TePr^i_2$) [30].

7. Conclusions

This review has shown that the synthesis of metallo-organic precursors for the deposition of refractory inorganic materials as films on a wide range of surfaces is a very active field. Important developments may confidently be expected in the future.

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Applied Surface Science 46 (1990) 5–8
North-Holland

Design and synthesis of CVD precursors to thin film ceramic materials

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Received 30 May 1990; accepted for publication 4 July 1990

The application of cyclic organometallic compounds as single source precursors for the chemical vapor deposition of materials such as AlN and SiC is discussed and new results relating to the decomposition of a novel SiC CVD precursor are presented. The decomposition of the cyclic carbosilane $[\mu\text{-}(CH_2)_2Si(CH_3)(H)Si(CH_3)(CH_2SiH_2CH_3)]$, (I) on a heated glassy carbon substrate in an ultra-high vacuum molecular beam system has been studied by pulsing the precursor molecule onto the surface and following the mass spectrum as a function of the substrate surface temperature. The evolution of CH_3SiH_2, C_2H_5 and CH_3 was evidenced, suggesting loss of excess carbon as C_1 and C_2 species.

1. Introduction

Although organometallic compounds have been used for well over twenty years in the chemical vapor deposition of inorganic thin films [1], efforts to specifically design and synthesize such compounds for use in CVD have only recently received significant attention [2]. For most MOCVD processes each element required in the final inorganic film is supplied individually in the form of a relatively simple molecular source, such as trimethylgallium and arsine in the case of GaAs deposition. Since these deposition processes generally yield inorganic compounds containing two or more elemental components, at least two molecular sources are required, usually in combination with a carrier gas such as hydrogen. Problems associated with chemical interactions between the molecular sources, their differing thermolysis and chemisorption behavior, as well as the complex flow dynamics and mixing in the CVD reactors, limits the applicability and adds to the cost of CVD processing; moreover, control of the composition, homogeneity and microstructure of the product thin films is often difficult.

The availability of suitable single-source precursors for these CVD processes may help to overcome some of the current limitations of CVD processing. Finally, the thermal instability of the substrate or the underlying device structure often presents severe limitations on the film deposition methodology, driving the search for thermal CVD precursors which will work effectively at lower substrate temperatures.

This need for lower temperature, single-component precursors for CVD processes is particularly acute in the case of materials such as aluminum nitride, silicon carbide and silicon nitride. The preparation of dense, uniform, and stoichiometric thin films of these highly refractory materials at temperatures less than 1000 °C has proven to be an especially challenging problem for thermal CVD processing [1].

We have been exploring the use of designed organometallic precursors for the CVD of these materials and have initiated studies of various cyclic compounds as potential precursors. In the case of AlN, our attention has focused on the use of dimethylaluminum amide, $[(CH_3)_2AlNH_2]_3$, a molecular compound whose structure contains six-membered $(AlN)_3$ rings, much like the $(AlN)_3$

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