

AD-A262 823



2

OFFICE OF NAVAL RESEARCH

GRANT N00014-88-K-0483

R & T Code 413n008

Technical Report No. 42

**Characterization of Copper Iodide Thin Films
Fabricated via
Laser Assisted Molecular Beam Epitaxy**

by

W. M. K. P. Weijekoon, M. Y. M. Lykтей, P. N. Prasad , & James F. Garvey*

Prepared for Publication
in
Journal of Applied Physics



Acheson Hall
Department of Chemistry
University at Buffalo
The State University of New York at Buffalo
Buffalo, NY
14214

93 4 09 062

April 3, 1993

93-07537



24P6

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 4/3/1993		3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE Characterization of Copper Iodide Thin Films Fabricated via Laser Assisted Molecular Beam Epitaxy				5. FUNDING NUMBERS R & T Code: 413n008 G N00014-88-K-0483	
6. AUTHOR(S) W.M.K.P. Wijekoon, M.Y.M. Lyktey, P.N. Prasad, and James F. Garvey					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept. of Chemistry, Acheson Hall State University of New York at Buffalo Buffalo, NY 14214				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #42	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. R. DeMarco/Dr. J. Pazik, Chemistry Division Office of Naval Research 800 N. Quincy St. Arlington, VA 22217				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) For the first time the technique laser assisted molecular beam epitaxy (LAMBE) has been used to fabricate a molecular film by reaction in a molecular beam. Molecular iodine vapor entrained into a stream of helium carrier gas was introduced via a supersonic expansion into the plasma plume of laser evaporated copper to produce copper iodide. Films were deposited on substrates that were situated about 3 cm downstream on the path of the molecular beam. The surface morphology of films depends greatly on the fluence of the incident laser beam and expansion conditions. Films grown at low laser powers show small surface inhomogeneities in their electron micrographs compared to the films that were grown at higher laser powers. Copper in the LAMBE films is found to be mainly in the Cu^+ state as characterized by electron spectroscopy for chemical analysis (ESCA). A comparison of the surface and structural properties of LAMBE films with that of a vacuum evaporated film suggests both films have similar lattice structures and compositions. It seems that LAMBE can be a powerful technique to deposit novel molecular and composite films for electronics and photonics.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	
				20. LIMITATION OF ABSTRACT UL	

Characterization of Copper Iodide (CuI) Thin Films Fabricated via Laser Assisted Molecular Beam Epitaxy

W. M. K. P. Wijekoon, M. Y. M. Lyktey, P. N. Prasad*, J. F. Garvey*

Photonics Research Laboratory and Department of Chemistry,

The State University of New York at Buffalo, Buffalo, New York 14214.

-Abstract-

For the first time the technique laser assisted molecular beam epitaxy (LAMBE) has been used to fabricate a molecular film by reaction in a molecular beam. Molecular iodine vapor entrained into a stream of helium carrier gas was introduced via a supersonic expansion into the plasma plume of laser evaporated copper to produce copper iodide. Films were deposited on substrates that were situated about 3 cm downstream on the path of the molecular beam. The surface morphology of films depends greatly on the fluence of the incident laser beam and expansion conditions. Films grown at low laser powers show small surface inhomogeneities in their electron micrographs compared to the films that were grown at higher laser powers. Copper in the LAMBE films is found to be mainly in the Cu^+ state as characterized by electron spectroscopy for chemical analysis (ESCA). A comparison of the surface and structural properties of LAMBE films with that of a vacuum evaporated film suggests both films have similar lattice structures and compositions. It seems that LAMBE can be a powerful technique to deposit novel molecular and composite films for electronics and photonics.

*Authors to whom correspondence should be made

Introduction

Thin films of high performance materials are currently of considerable interest for application in advanced technologies such as photonics, electronics, and superconductors¹⁻⁶. Many integrated optics, micromechanics, and semiconductor devices rest on their nanostructure control of the film. There are a number of well known physical and chemical thin film fabrication techniques such as radio frequency (RF) magnetron sputtering, chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) that can be used to deposit thin layers of metal and semiconducting superlattices. However, there are various experimental difficulties and disadvantages associated with all thin film fabricating techniques⁷. For example, MBE allows precise control of the deposition process, permitting layer by layer deposition of the materials, but the compositional control of the films is difficult with both CVD and MBE. Also, in the case of metal oxides the typical oxygen pressure necessary for the growth of the film not only makes it difficult to control the composition of the film, but also puts severe constraints on the utilization of ultrahigh vacuum conditions. Clearly, the high oxygen pressure is problematic in planar magnetron sputtering since the plasma generated O_2 can infringe on the sample and, thereby, alter its composition. Thus an ion infringement can be minimized by changing the geometry between the target and the substrate, however, in such situations the efficiency of the film deposition is also drastically reduced.

Pulsed laser deposition⁸⁻¹⁷ and, in particular, laser assisted molecular beam epitaxy (LAMBE)¹⁸, is a promising technique for deposition of high quality thin films of materials such as metals and metal oxides in that it overcomes many of the above indicated problems. Pulsed laser deposition has already been used to fabricate thin films of multielement superconductors with the preservation of the stoichiometry of the target in the film¹⁹. This demonstrates the significantly simplified deposition of complex materials with the assistance of the pulsed lasers. In an attempt to fabricate high quality thin films of novel multifunctional composite materials

for photonics and electronics we have initiated a research project utilizing a modification of the LAMBE technique. Our approach involves two major steps. First, the bulk target material is ablated with the use of a tightly focused pulsed laser beam. Second, during ablation a rapidly expanding gas pulse is introduced into the plasma plume (20,000 K) of ablated materials. This gas pulse subsequently carries the evaporated materials through the expansion nozzle and delivers to the substrate downstream from the molecular beam. The turbulent mixing of the carrier gas with plasma plume produces a very homogenous molecular beam density which in turn results in the generation of a very uniform film. Moreover, the carrier gas can chemically interact with the ablated materials thereby creating new chemical products which can be deposited on the substrate. This chemistry occurs within the high temperature of the plasma, well away from the substrate.

Some of the distinct advantages of the LAMBE are that (i) evaporation of the target occurs within a short laser pulse during which a high temperature plasma is formed. Therefore, the process can be inherently self-cleaning (ii) the substrate is not in contact with the plasma so the ion bombardment on the growing film is negligible (iii) the film can be deposited under a wider range of experimental conditions such as varying rate, pressure and temperature and (iv) by using different carrier gases and different seeding materials the chemistry of the film can be judiciously controlled to make novel composite materials.

In this paper we report the fabrication and characterization of copper iodide (CuI) films that were directly grown by the LAMBE technique using metallic copper and iodine vapor. In our preliminary experiment CuI was selected as the LAMBE molecule due to the following reasons. Copper is one of the metals that can be ablated very easily even with a low laser fluence. Also, LAMBE has been previously employed to fabricate thin films of copper and copper oxides. Therefore, some of the parameters that are vital to fabrication of uniform films have been previously formulated¹⁸. Furthermore, iodine has a large enough vapor pressure at the

room temperature so that it can be entrained into the carrier gas very easily. The CuI films are characterized by electron spectroscopy for chemical analysis (ESCA), field emission scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS), Raman and uv-visible spectroscopic techniques. For comparison, we deposited CuI films via vacuum evaporation and the structural properties and surface morphology of these reference films are compared with that of the LAMBE films. These two types of CuI films exhibit very similar structural properties.

Experimental Aspects

The LAMBE apparatus consists of a modified *Smalley-type* source^{20,21} in which gas phase aggregates of the target are generated by pulsed laser ablation followed by supersonic expansion (figure 1). The cluster source is fitted to a pulsed molecular beam valve (*Newport BV-100*) with a 0.5 mm nozzle. The target (0.5" copper rod) was connected to a stepper motor driven shaft which could rotate and translate simultaneously. The copper rod was ablated by a tightly focused output ($\lambda=248$ nm) of a KrF excimer laser (*Lambda Physik EMG150*). The experimental geometry is such that the direction of the incident beam is mutually perpendicular to the axis of the molecular beam and the rotational axis of the target. The movement of the copper rod was synchronized with the laser pulses to ensure that each time ablation occurred at a new location on the surface of the target. Typical laser power levels were ~ 200 mJ/pulse with a pulse duration of 20 ns and a repetition rate of 5 Hz.

Coincident with each laser pulse, a gas pulse (~ 1 ms in duration) was introduced into the source at a predetermined delayed time of 450 μ s (using a digital delay generator *EG & G 9650*), so that the ablated material is entrained into the gas pulse and carried into the vacuum chamber through the expansion nozzle. The cluster source is mated to the deposition chamber through an expansion region (~ 12 mm diameter and 1.5 cm long) with the substrate situated ~ 3

cm downstream from the molecular beam. Typical operational pressure of the vacuum chamber fluctuated between $3-6 \times 10^{-5}$ torr when the backing pressure of the carrier gas is ~ 40 psi.

For the fabrication of CuI films, iodine vapor was introduced into the ablated metal plasma in a stream of helium gas. Crystalline iodine at room temperature was held in a pyrex U-tube, one end of which was connected to the pressurized helium gas line, the other end being connected to the inlet of the pulsed beam valve. The films were grown either on precleaned teflon substrates (for ESCA analysis) or on uv-silica glass (*Esco Products*) substrates. A typical thickness of $0.2 \mu\text{m}$ was estimated by edge-on SEM for a film which was run for a period of ~ 3 hours. This growth rate is much smaller than that estimated for metallic copper films which were grown in the presence of the same carrier gas¹⁶. One possible reason for this anomaly is that iodine vapor entrained in He may tend to cool the plasma temperature thereby lower the efficiency of ablation.

For the preparation of vacuum evaporated films, CuI purchased from *Aldrich Chemicals* was used without further purification. The substrate was situated inside a custom built vacuum chamber which could be pumped down to a base pressure of 10^{-6} Torr. The CuI powder was held in a glass boat and slowly heated at a rate of $\sim 10^\circ/\text{minute}$. The reference films were deposited onto unheated substrates at a rate of $\sim 10 \text{ \AA}/\text{minute}$.

The surface analysis of the LAMBE films was carried out with a *Perkin Elmer Physical Electronics PHI 5100 ESCA* instrument under high vacuum conditions (7×10^{-8} torr). Unmonochromatized MgK_α X-rays (1253.6 eV) from a dual anode were used as the excitation source and a hemispherical analyzer with a single channel channeltron electron multiplier as the detecting element. Pass energies of 89.45 eV for low resolution spectra and 35.75 eV for high resolution spectra were used. The ESCA survey spectrum was recorded at a take-off angle of 45° , whereas the elemental high resolution spectra were collected at two different take-off angles, namely 15° and 90° . The overall resolution of the ESCA system is ~ 2 eV.

The SEM/EDXS studies were performed at the university biomaterial center with a *Hitachi S-800* SEM system and a *PGT IMIX* EDXS system. Electron micrographs were taken at 25 keV filament voltage and tilt angle was 45° . For thickness measurements films were snapped in half and examined edge-on by SEM. A deposition rate of $\sim 0.06 \mu\text{m}/\text{hour}$ was estimated for CuI films.

Raman spectra of thin films and the CuI powder were recorded with a spectrometer that consists of a continuous wave Ar ion laser (*Spectra Physics 2020*) operating in the TEM_{00} mode. The laser beam ($\lambda=514.5 \text{ nm}$) was focused onto the samples and the scattered light was collected with a 15 cm focal length lens and focused onto the entrance slit of a *Czerny-Turner* double monochromator (*Spex 1403*). The dispersed light was focused onto a photocathode of a thermoelectrically cooled photomultiplier tube (*ITT FW 130*). The signal from the PMT was fed into a digital electrometer (*Keithley 614*) and the electrometer output was read by a PC computer which also controls the monochromator. The power levels deposited on the samples were $\sim 100 \text{ mW}$.

Observations and Discussion

The surface morphology, rate of deposition and the chemical composition of the LAMBE films largely depend on the nature of the carrier gas as well as on the fluence of the incident laser¹⁸. When a pure metallic target is ablated in the presence of inert carrier gases (such as He, N_2 and Ar) metallic thin films are generated. When reactive carrier gases (such as O_2) are used metal oxide films are generated. The SEM pictures of LAMBE films that are grown under high incident laser powers show the presence of scattered island-like structures on the film surface regardless of the nature of the carrier gas. However, in films that were deposited with relatively low laser powers such islands were essentially absent. These results can be rationalized in terms of the average aggregate size grown within the molecular beam expansion.

As characterized by SEM, vacuum evaporated CuI films and LAMBE films of CuI that were grown at high laser powers have approximately the same surface morphology (figure 2). However, the LAMBE films that were grown with low laser powers exhibit less surface inhomogeneities compared to that of the above films. Nevertheless, in the material contrast image some surface inhomogeneities in composition are visible. The EDX spectra of the films show that the prevailing elements on the surface are Si (substrate), Cu and I (figure 3). A closer examination of the scattered white particles shown in the electron micrograph of figure 2c, by EDX spectroscopy, reveals that these particles are composed of copper and iodine. The presence of such islands on the surface of the film indicates clustering of CuI in the process of the film growth. These large clusters may result from the ejection of microscopic liquid droplets from the target and/or due to the formation of large clusters by condensation of monomers while still in flight.

The ESCA survey (low resolution) spectrum of the LAMBE film also shows that the prevailing elements on the film surface are Cu and I (figure 4). The binding energy scale of the ESCA spectrum was calibrated by assigning 284.8 eV for C 1s signal²². As seen in the elemental high resolution ESCA spectrum (figure 5) of the copper 2p doublet region, there are no prominent satellite structures which are characteristic of Cu (II)²³⁻²⁷. The satellite peaks originate from the *shake-up* transitions due to the *charge-transfer* from the ligand to the 3d shell of copper²⁴. Such *charge-transfer* is forbidden in Cu⁺ compounds because of the filled 3d shell. Therefore, the absence of such satellites in the high resolution ESCA spectrum confirms that Copper in the LAMBE film is not in the form of Cu⁺².

CuI is a semiconductor having the *zincblende* structure at ambient temperature and pressure²⁸⁻³¹. Disorder in the crystal lattice increases with increasing temperature and CuI undergoes a phase transition from *zincblende* structure (γ -phase) to *wurtzite* structure (β -phase) around 370 °C. Further increase in temperature transforms *wurtzite* structure to *face centered*

cubic structure (α -phase) around a temperature of 410°C .³² However, at room temperature and pressure the uv absorption spectrum and Raman spectrum of CuI can be interpreted in terms of the *zincblende* structure³³⁻³⁶.

UV absorption spectra of *zincblende* type semiconductors show striking similarities³⁵. The lowest energy absorption edge due to transitions at $k = 0$ shows a splitting resulting from the spin-orbit interaction of the constituent atoms. The next absorption edge originates from direct transition at a point in the (111) direction of k space³⁵. However, the absorption spectra of copper halides show a deviation from the systematics of that of other *zincblende* type semiconductors. Because of the weakly bound 3d electrons the first absorption edge occurs at much lower energies in copper halides than that expected for many other *zincblende* type semiconductors³⁷.

As shown in figure 6, the uv spectrum of the LAMBE film is essentially identical to that of the vacuum evaporated CuI film. The absorption peak at 405 nm (3.06 eV) of the uv spectrum is due to the lowest *excitonic* excitation of electrons in the four-fold valance band (Γ_8) and the peak at 335 nm (3.7 eV) has been assigned to the transition between the two-fold (Γ_7) spin-orbit split-off band and the *excitonic* ground state. The peak at 260 nm (4.76 eV) has been assigned to a saddle point in energy difference between the valance and conduction band occurring for k in the (111) direction somewhere inside the *Brillouin zone*³⁸. The exciton peak at 3.06 eV splits into a doublet at low temperatures due to the internal strain arising from differential thermal contractions between the film and the substrate^{35,36}. Also, the presence of traces of *wurtzite* and *hexagonal* type CuI gives rise to additional exciton peaks in the spectral range 400 - 300 nm. The absence of such exciton peaks in the uv spectrum of the LAMBE film and the vacuum evaporated CuI film indicates that both the films possess the *zincblende* type structure.

In thin films, CuI crystallites are preferentially oriented with the (111) axis perpendicular

to the plane of the film^{35,37}. The Raman spectra of CuI in its all three phases have been reported by Burns and coworkers³². In the γ -phase (*zincblende*) TO (transverse optical) phonon mode appears at 126 cm^{-1} in the first-order Raman spectrum. As shown in figure 7, Raman spectrum of the vacuum evaporated film is essentially identical to that of the LAMBE film. In both Raman spectra the TO mode appears around 119 cm^{-1} .^{39,41} The energy of this TO mode is in reasonable agreement with the earlier experiments^{32,39} which reported it at 124 cm^{-1} and 126 cm^{-1} . Based on the results of our uv and Raman spectroscopic data, it is reasonable to assume similar orientations of CuI crystallites in these two types of films.

Conclusions

Laser assisted molecular beam epitaxy provides a flexible means to fabricate thin films of a pure target material as well as thin films of a chemically modified target material. The chemical composition of these films can be largely varied by incorporating different seeding materials into the ablated plasma plume. Surface morphology of the LAMBE films can be changed by using different carrier gases as well as incident laser power. Moreover, the flexibility in selecting a variety of seeding materials and targets provides a very effective means to modify the chemistry of the film, so it can be specifically tuned for the application of interest.

Acknowledgement

W. M. K. P. Wijekoon acknowledges Patrick Schamberger for the help in the ESCA experiment and Peter Bush for many discussions on SEM/EDXS experiments. This research was supported by the National Science Foundation solid state chemistry program (#DMR9213907), Office of Naval Research, and the A. P. Sloan Foundation.

References

1. *Clusters and Cluster-Assembled Materials*, eds: Robert S. Averback, Jerzy Bernholc and David L. Nelson, Materials Research Society Symposium Proceedings, vol. **206**, Pittsburgh, (1991).
2. *Chemical Processing with Lasers*, Ed: D. Bauerle, Springer Series in Material Science, vol. **1**, Springer-Verlag, New York (1986).
3. *Laser Processing of Thin Films and Microstructures*, Ed: Ian W. Boyd, Springer Series in Material Science, vol. **3**, Springer-Verlag, New York (1987).
4. *Beam Epitaxy-Crystallisation of Semiconductor Film From Atomic and Molecular Beams*, Eds: G. Benedek, T. P. Martin and G. Pacchioni, Springer Series in Material Science, vol. **7**, Springer-Verlag, New York (1987).
5. A. Ulman, *An Introduction to Ultra Thin Organic Films from Langmuir-Blodgett to Self-Assemblies*, Academic, San Diego, 1991.
6. *Langmuir-Blodgett Films*, Ed: Gareth Roberts, Plenum, New York, 1990.
7. X. D. Wu, S. R. Foltyn, R. C. Dye, A. R. Garcia, N. S. Nogar and R. E. Muenchausen, *Thin Solid Films*, **218**, 310, (1992).
8. M. Moallem, D. R. Olander, M. Balooch and M. J. Fluss *J. Vac. Technol. A*, **10**, 3292, (1992).
9. O. Rist and P. T. Murray, *Fresenius J. Anal. Chem.* **341**, 360, (1991).
10. J. P. Bucher, D. C. Douglass and L. A. Bloomfield, *Rev. Sci. Instrum.* **63**, 5667, (1992).
11. E. R. Fisher, P. Ho, W. G. Breiland and R. J. Buss, *J. Phys. Chem.* **96**, 9855, (1992).
12. F. Sajovec, P. M. Meuffels and T. Schober, *Thin Solid Films*, **219**, 206, (1992).
13. H. Haberland, M. Karrais, M. Mall and Y. Thurner, *J. Vac. Sci. Technol. A*, **10**, 3266,

- (1992).
14. C. J. Peng, S. B. Krupanidhi, *Thin Solid Films*. **219**, 162, (1992).
 15. S. Otsubo, T. Maeda, T. Minamikawa, Y. Yonezawa, A. Morimoto, T. Shimizu, *Jpn. J. Appl. Phys.* **29**, L133, (1990).
 16. G. koren, R. J. Baseman, A. Gupta, M. I. Lutwuche, R. B. Laibowitz, *Appl. Phys. Lett.* **55**, 2450, (1989).
 17. X. D. Wu, A. Tinman, T. Venkatesan, C. C. Change, E. W. Chase, P. Barbouse, J. M. Tarascon, B. Wilkens, *Appl. Phys. Lett.* **52**, 754, (1988).
 18. W. J. Herron, J. F. Garvey, in *Clusters and Cluster-Assembled Materials*, eds: Robert S. Averback, Jerzy Bernholc and David L. Nelson, Materials Research Society Symposium Proceedings, vol. **206**, Pittsburgh, (1991).
 19. D. Dijkkamp, T. Venkatesen, X. D. Wu, A. Shaheen, N. Jiswari, Y. H. Min-Lee, W. L. Mclean, M. Croft, *Appl. Phys. Lett.* **51**, 619, (1987).
 20. D. E. Powers, H. G. Hansen, M. E. Geusic, A. C. Pulu, J. B. Hopkins, T. G. Dietz, MM. A. Duncan, P. R. R. Langridge-Smith, R. E. Smalley, *J. Phys. Chem.* **86**, 2556, (1982).
 21. D. E. Powers, S. G. Hansen, M. E. Geusic, P. L. Michalopoulos, R. E. Smaalley, *J. Chem. Phys.* **78**, 2866, (1983).
 22. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, *Hand Book of X-ray Photoelectron Spectroscopy*, (Perkin-Elmer, 1979).
 23. B. Wallbark, C. E. Johnson, I. G. Main, *J. Phys. C.* **6**, 1493, (1973).
 24. K. S. Kim, *J. Electron. Spectrosc. Related Phenomena.* **3**, 217, (1974).
 25. J. C. Klein, A. Proctor, D. M. Hercules, J. F. Black, *Anal. Chem.* **55**, 2055, (1983).
 26. T. H. Fleisch, G. J. Mains, *Appl. Surf. Sci.* **10**, 51, (1982).
 27. T. Roberts, M. Bartel, G. Offergeld, *Surf. Sci.* **33**, 123, (1972).
 28. P. D. Martzen, W. C. Walker, *Phys. Rev. B.* **21**, 2562, (1980).

29. Z. Vardeny, O. Brafman, Phys. Rev. B. **19**, 3290, (1979).
30. T. Marasashi, T. Koda, J. Phys. Soc. Jpn. **40**, 747, (1976).
31. T. Fukumoto, K. Tabuchi, S. Nakashima, A. Mitsuishi, Opt. Commun. **10**, 78, (1974).
32. G. Burns, F. H. Dacol, M. W. Shafer, R. Alben, Solid State Commun. **24**, 753, (1977).
33. P. D. Martzen, W. C. Walker, Solid State Commun. **28**, 171, (1978).
34. S. Lewonczuk, J. G. Gross, M. A. Khan, J. Ringeissen, Phys. Stat. Sol. B. **83**, 161, (1977).
35. M. Cardona, Phys. Rev. **129**, 69, (1963).
36. T. Sander, A. Daunois, J. L. Deiss, J. C. Merle, Solid State Commun. **51**, 323, (1984).
37. I. D. Bedikyan, V. K. Miloslavskii, L. A. Ageev, Opt. Spectrosc. **49**, 167, (1980).
38. D. Brust, J. C. Phillips, F. Bassani, Phys. Rev. Lett. **9**, 94, (1962).
39. J. E. Potts, R. C. Hanson, C. T. Walker, C. Schwab, Solid State Commun. **13**, 389, (1973).
40. B. Henniom, F. Moussa, B. Prevot, C. Carabatos, C. Schwab, Phys. Rev. Lett. **28**, 964, (1972).
41. J. N. Plendl, A. Handi, J. Claudel, Y. Henninger, G. Morlet, P. Strimer, L. C. Mansur, Appl. Opt. **5**, 397, (1966).

Figure Captions

Figure 1. Schematics of the LAMBE apparatus. Iodine was introduced into the ablated metal plasma plume by entraining into a stream of He carrier gas.

Figure 2. SEM pictures of (a) vacuum evaporated CuI film (b) LAMBE film of CuI grown at higher laser power (c) LAMBE film of CuI grown at lower laser power. Films are deposited onto uv-silica glass substrates.

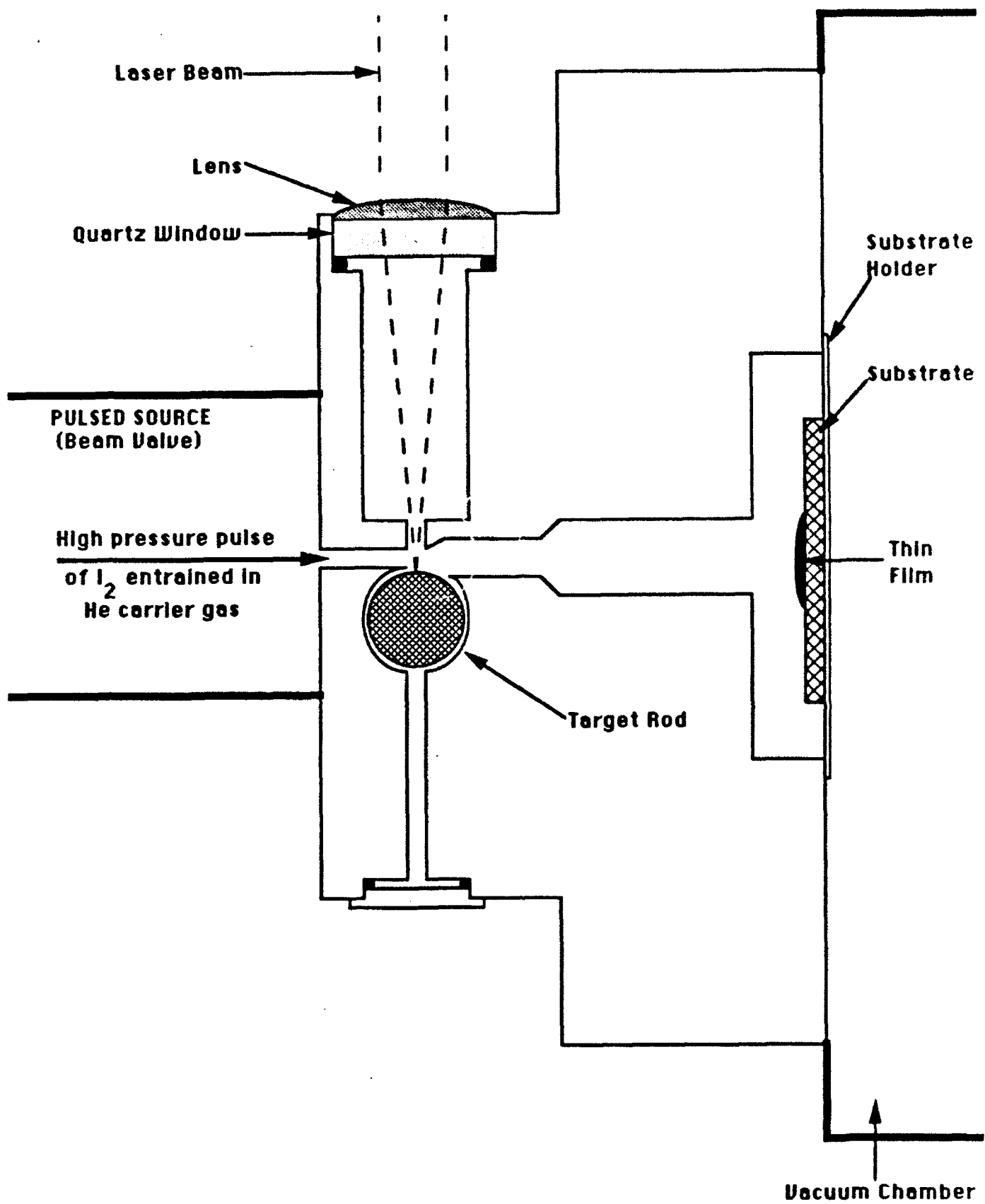
Figure 3. EDX spectrum of the white particle shown in figure 2(c). Thickness of the film $\sim 1000\text{\AA}$ as determined by SEM.

Figure 4. The ESCA survey (low resolution) spectrum of the LAMBE film. Pass energy is 89.45 eV.

Figure 5. Elemental high resolution ESCA spectrum Cu 2p doublet region after calibrating with respect to C 1s signal (284.8 eV).

Figure 6. Absorption spectra of (a) LAMBE film, (b) vacuum evaporated film. Spectra were recorded by using a bare substrate as the reference.

Figure 7. Raman spectra of (a) LAMBE film, (b) vacuum evaporated film. Spectrum (a) contains 125 scans and spectrum (b) contains 15 scans. Spectra have been vertically offset for clarity.



- Figure 1
Wuexoon et al

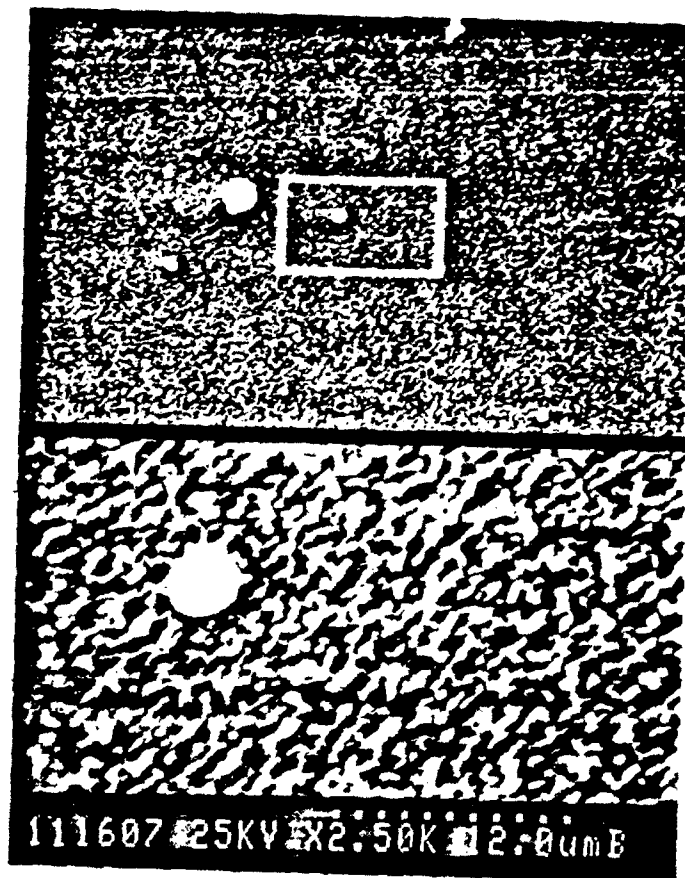
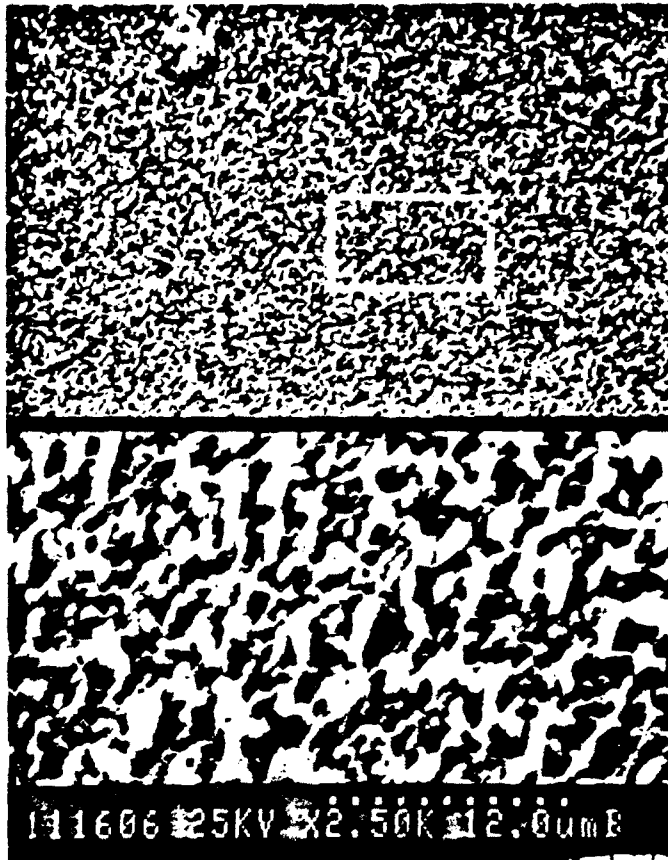


Figure 2(a) -
Wijekoon, et al



- Figure 2(b)
Nijekoon et al.

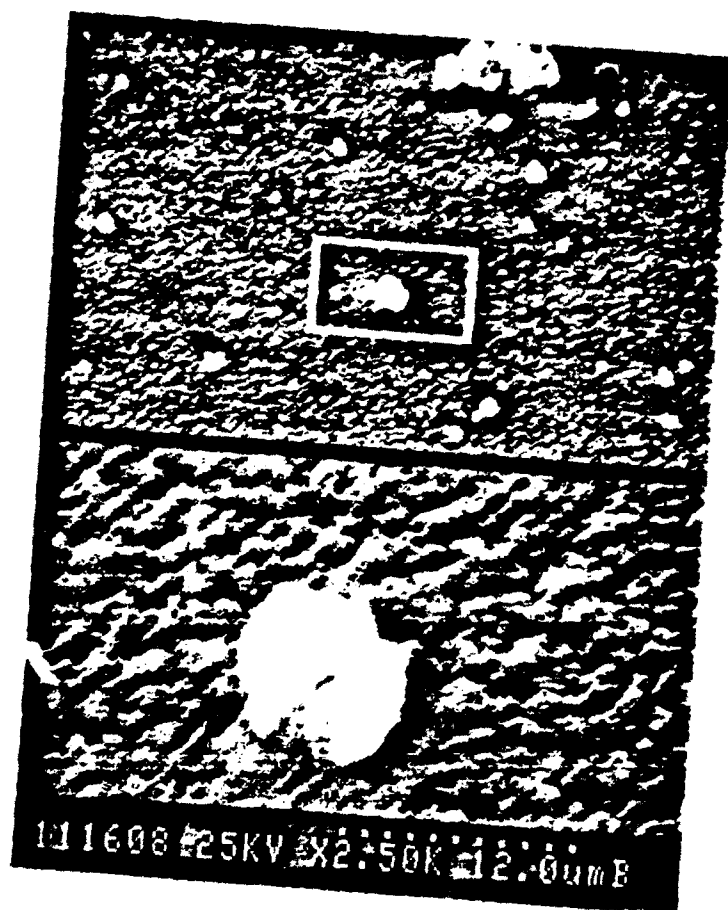
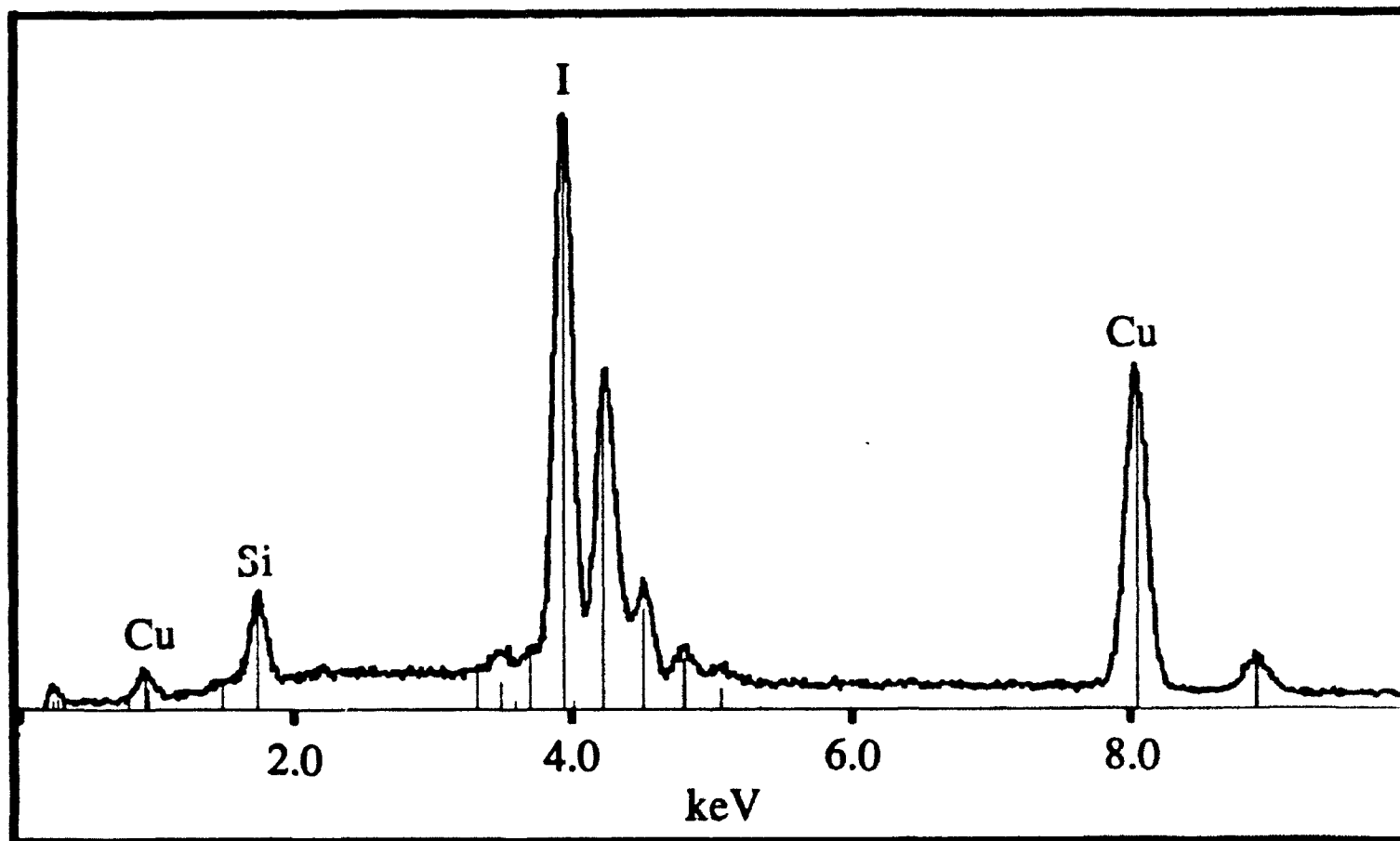
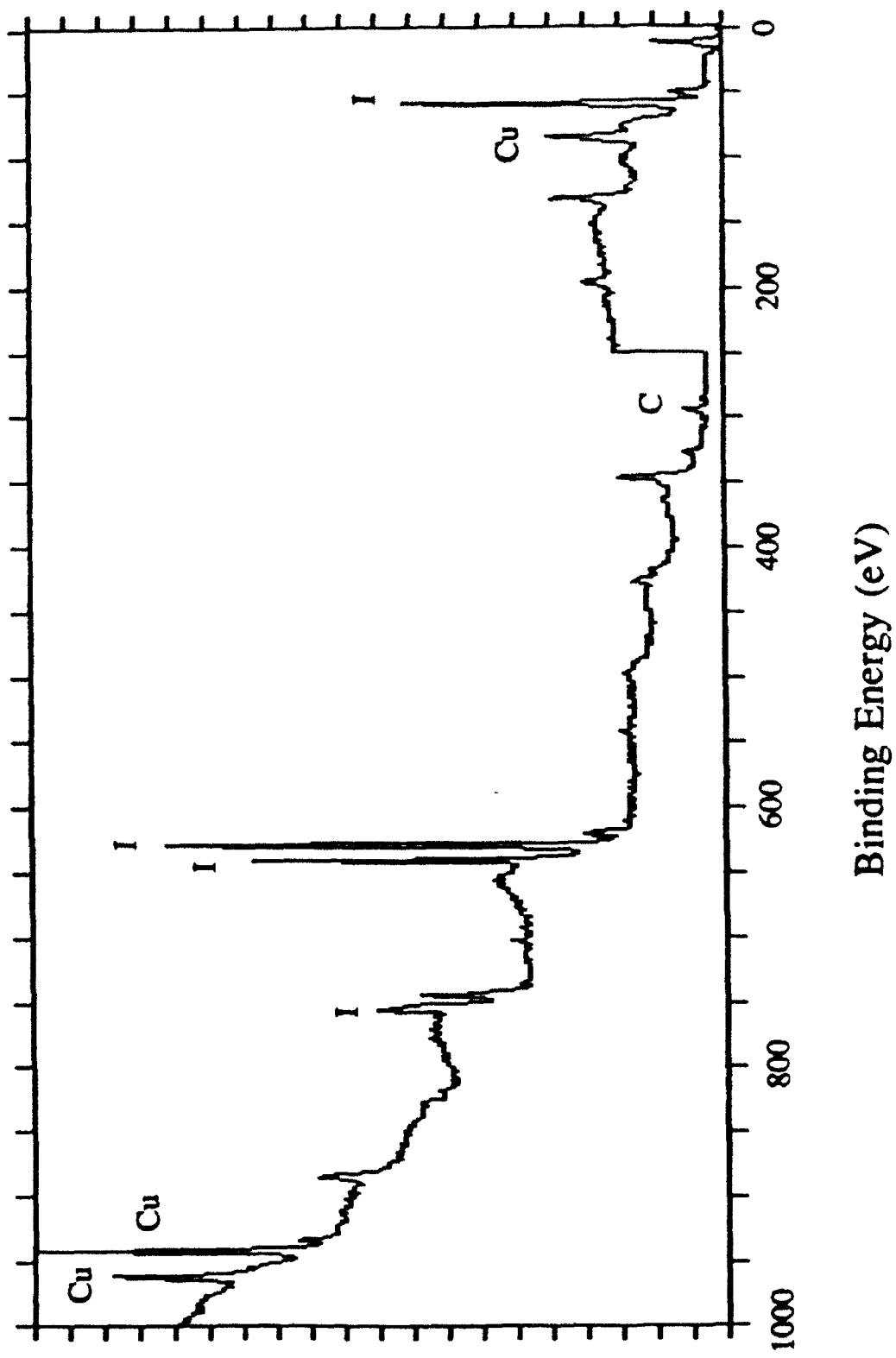


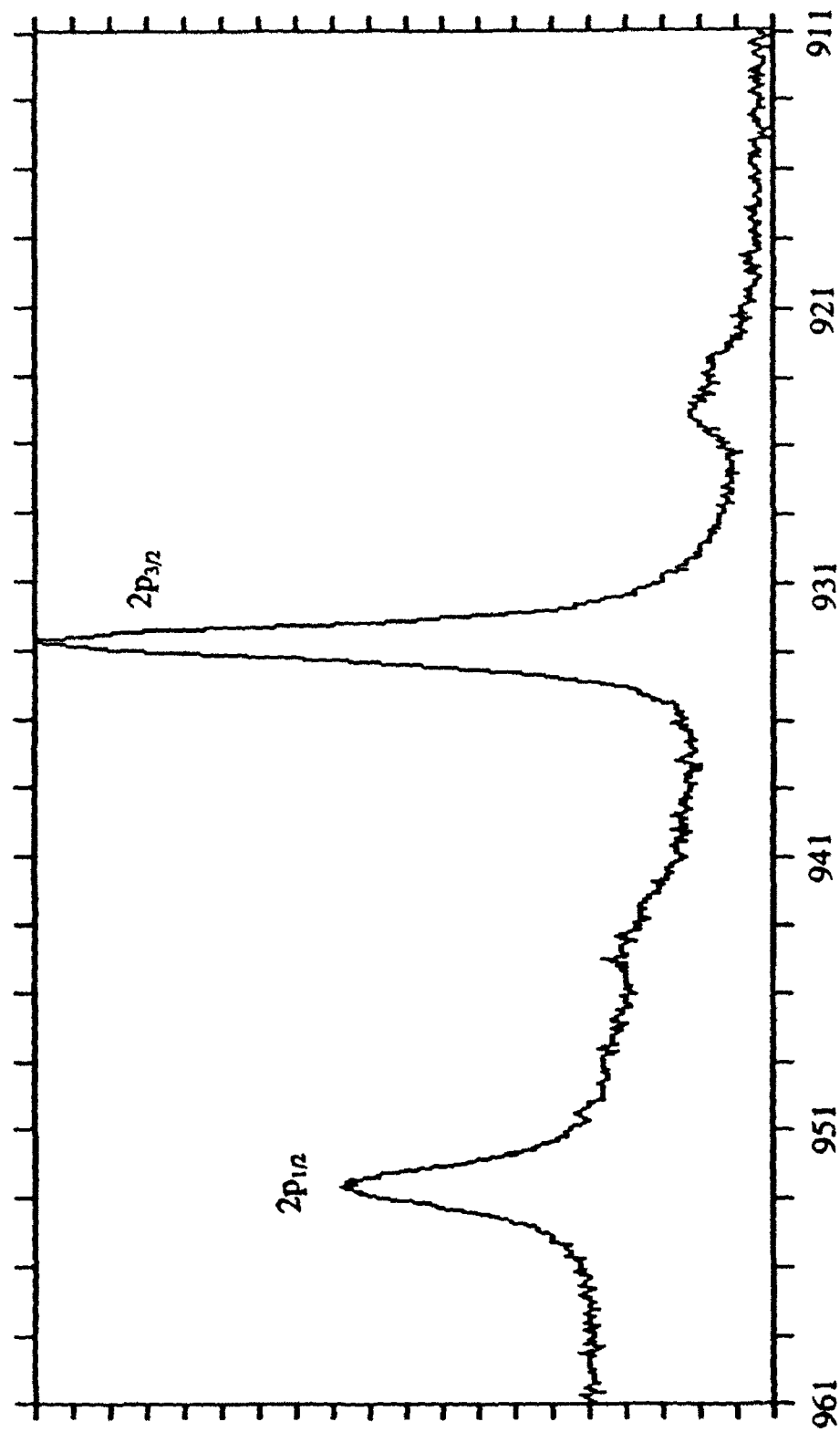
Figure 2(c)
Wijekoon et al.



- Figure 3
Wijekoon et al.

Figure 4





Binding Energy (eV)

Figure 5
Unknown et.al

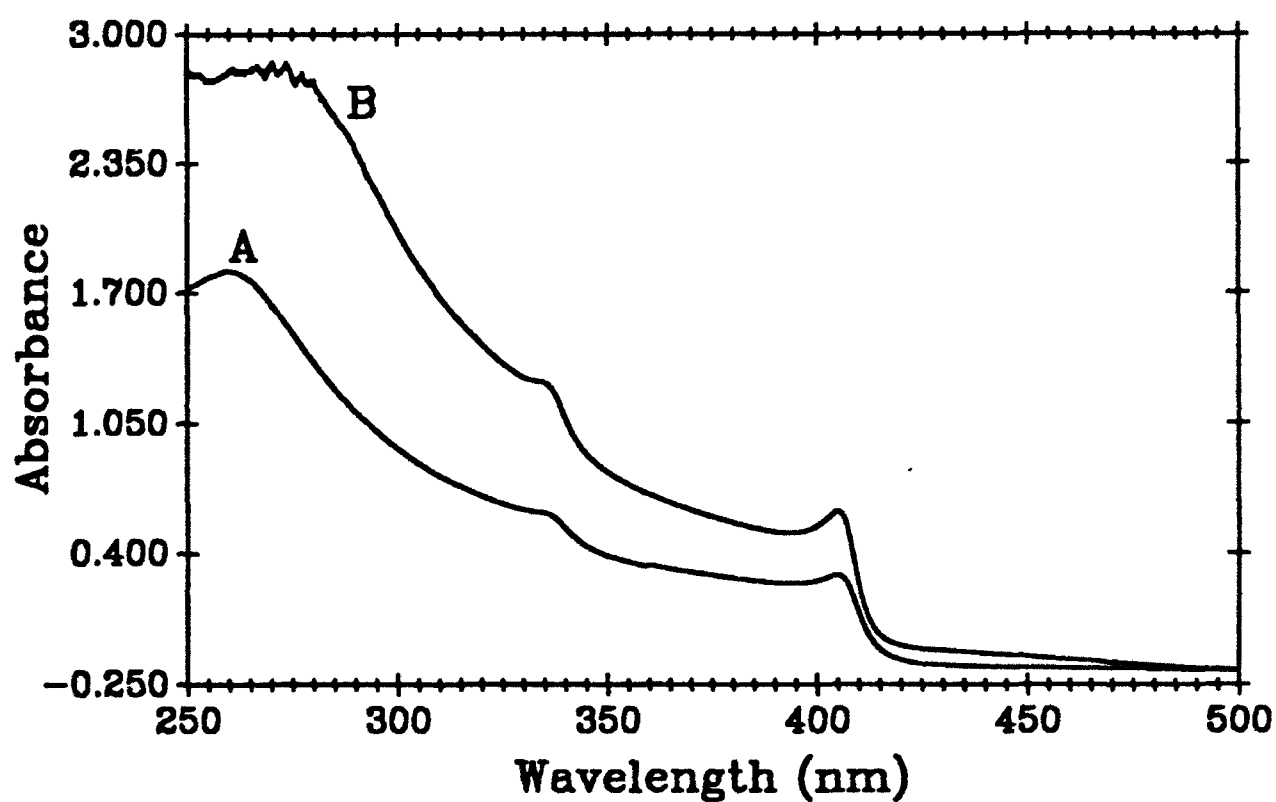
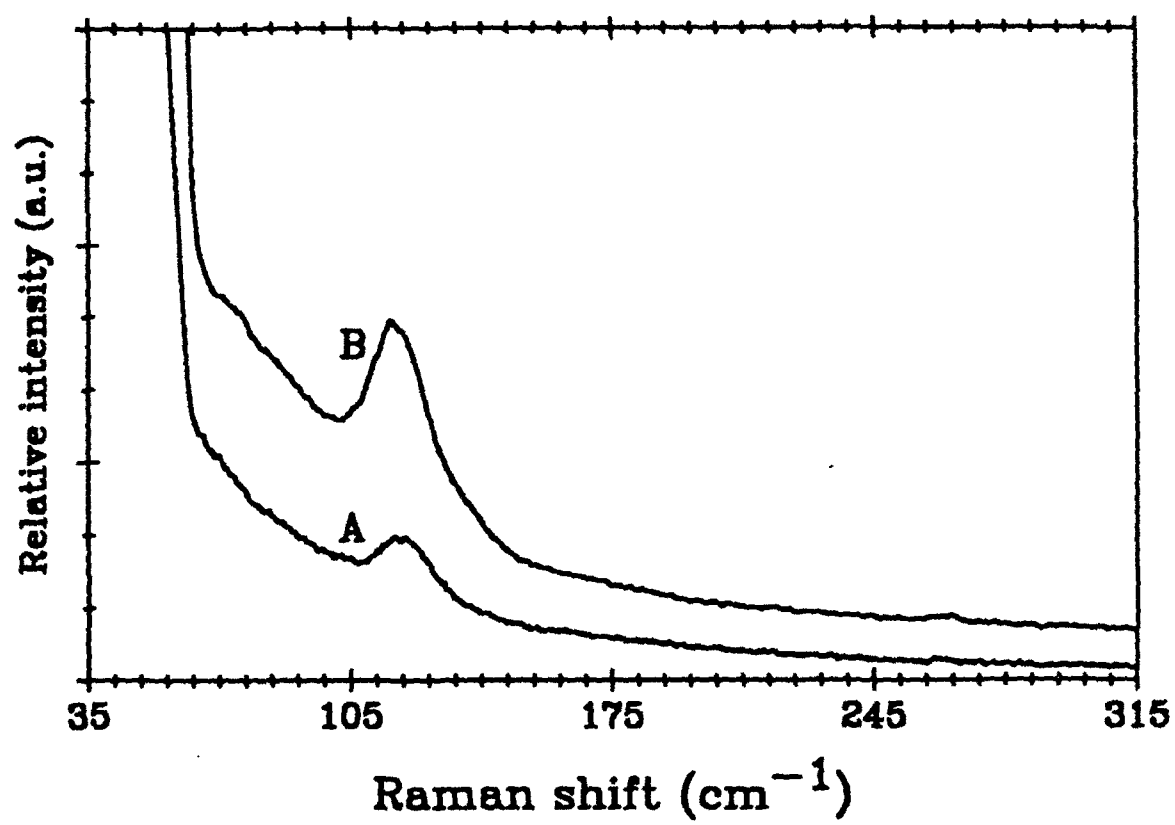


Figure 6
Wijekoon et al



- Figure 7
Wijetoon et al