Electrical Properties of Metal/Langmuir–Blodgett (Polymeraldine Base) Layer/Metal Devices

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SYNOPSIS

Metal-insulator–metal structures have been fabricated by sandwiching polyemeraldine base Langmuir–Blodgett (LB) films between metals like silver and indium vacuum-deposited onto indium-tin-oxide (ITO) glass. These devices have been found to exhibit insulating properties in the absence of a metal oxide layer. Current (I)–voltage (V) and capacitance (C)–voltage (V) measurements have been carried out on such devices. It is seen that these devices show rectification behavior at about 3 V for both forward and reverse bias conditions. However, at low voltages, nonlinear and asymmetric behaviors have been observed, whereas plot of log 1 versus $V^{1/4}$ indicates linear characteristics at high fields. The value of the barrier height has been found to be about 1.2 V in agreement with literature, implying Schottky behavior. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

The miniaturization of microelectronic devices based on organic materials has demanded much attention.[1,2] Recently, the organic molecules with dimension that of a single molecule have been focused for fabrication of a molecular electronic device (MED).[3,4] Compared to the bulk properties, it is the molecular properties that are known to govern the functioning of an MED. In this regard, the Langmuir–Blodgett (LB) technique currently represents one of the most versatile thin film processing route available for fabricating desired molecular electronic devices using electroactive polymer materials.[5–8]

Many investigations pertaining to use of LB layer for the fabrication of desired electronic devices have been conducted.[9–12] Most of the earlier work has been concerned with the deposition of LB layers of fatty acids onto inorganic semiconductors in order to passivate the surface or to modify the band bending in the semiconductors.[13]

Metal insulator–metal (MIM) devices based on fatty acids have been fabricated recently.[14,15] MIM is a convenient structure for a number of applications, such as switching, memory devices, electroluminescent displays, photovaltaic energy conversion, and microwave detection.[16,17] The numerous studies pertaining to rectification in LB films of conducting polumeric solids have been conducted.[18,19] Amongst the various conducting polymers, polyaniline has become the subject of increasing interest due to its increasing high charge capacity, good environmental stability, and excellent optical and electrical properties.[18–20] The deposition of quasi-ordered layers of polyaniline have been reported recently by Ram et al.,[21] and Misra et al.,[22] respectively.

In the present manuscript, polyemeraldine LB films have been sandwiched between metal (silver, indium) and metal vaccum deposited onto indium-tin-oxide glass. An attempt has also been made to investigate the mechanism of conduction in these MIM structures.

EXPERIMENTAL

The emeraldine base form of polyaniline has been chemically synthesized by oxidative polymeriza-

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Journal of Applied Polymer Science, Vol. 63, 141–145 (1997)
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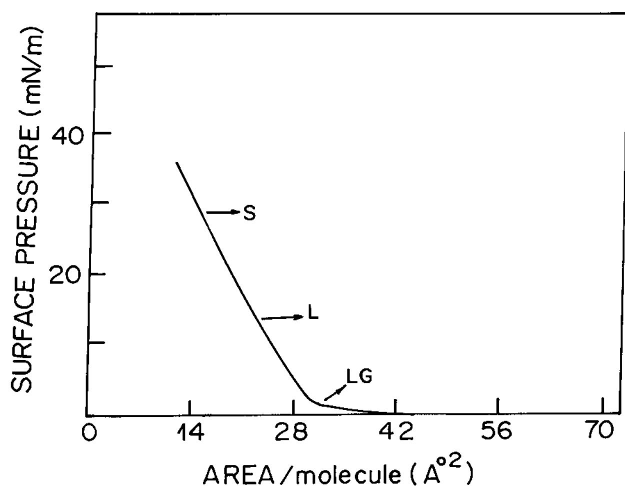

Figure 1 Pressure area isotherm of polyemeraldine base monolayer at 22°C.

tion of aniline in ammonium perdisulphate $[(NH_4)_2\ S_2O_3]$ under controlled conditions.[23] The dark green precipitate is filtered and is subsequently washed with methanol and dried over P_2O_5. The green powder thus obtained is emeraldine salt. The emeraldine salt is treated with water and acetone and is vacuum dried for about 24 h to obtain the deprotonated form of polyaniline (emeraldine base). Polyaniline is dissolved in a solvent containing 60% of $CHCI_3$ in N-methyl 2-pyrrolidinone (NMP). Further, 0.1 mg of emeraldine base (EB) is dissolved in a mixture of $CHCI_3$ and NMP and is sonicated for about 30 min. The resultant solution is filtered prior to being used for obtaining desired LB films.

LB film deposition has been carried out using the Joyce–Loebl LB trough (model 4). The pressure area isotherms of various Langmuir monolayers of polyemeraldine base (PEB) have been performed at a barrier compression speed of 0.5 cm^2/mol/min at 22°C. The pH of deionized water contained in the LB trough is maintained at 7. LB films of PEB have been deposited on silver, indium-tin-oxide, and silver glass plates, respectively. The effective electrode area of vacuum deposited metal (Ag) electrode onto LB (PEB) films is about 10^{-3} cm^2. Initially, direct current conductivity measurements been made in MIM configuration of PEB LB films. The inplane conductivity of PEB has been estimated to be about 5×10^{-3} s/cm at room temperature using experimentally measured thickness of about 8.0 Å. Since the very high field in the desired MIM devices based on LB monolayers could perhaps be "near breakdown" following the application of bias, we restricted our studies to the use of about 40 LB monolayers. Current (I)–voltage (V) and capacitance (C)–voltage (V) measurements have been carried out using Keithley electrometer (model 617) and an impedance analyzer (model HP 4192A), respectively.

RESULTS AND DISCUSSION

A typical pressure area isotherm obtained for emeraldine base at 22°C dissolved in a mixture of NMP and chloroform (40% of NMP and 60% of CHc13) is shown in Figure 1. The nature of pressure area isotherm (Fig. 1) is similar to that obtained for poly 2-decyloxy aniline. It has been found that solid phase condensation occurs at a surface pressure of 25 mN/M around a molecular area of 16 A^{o2}. Besides this, it can be clearly seen that liquid gas (LG) condensation begins at about the molecular area of 36 A^{o2}. It appears that the observed small change in the liquid to solid (L-S) phase may perhaps be due to the onset of a second-order phase transition. However, such monolayers (conductivity about 5×10^{-3}s/cm) have been utilized for the fabrication of desired MIM devices.

The insert in Figure 2 shows the variation of

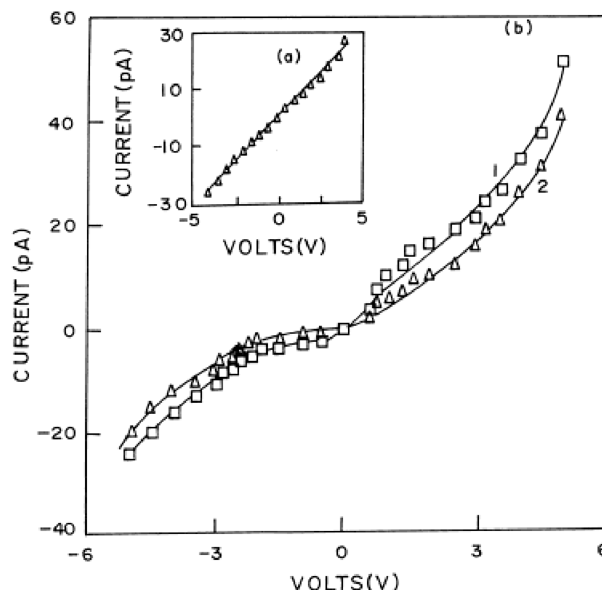

Figure 2 Insert shows current (I) versus voltage (V) characteristics for Ag/41 layers PEB LB films/Ag (curve 1); In/41 layers PEB LB films/Ag (curve 2); and ITO/41 layers PEB LB layers PEB LB film/Ag (curve 3) structures.

current (I) with voltage (V) for a silver (Ag)/41 PEB LB monolayers/silver (Ag) structure. It can be seen that the I-V characteristics are both linear and symmetric, indicating the tunneling of electrons on application of bias voltage. It is known that silver makes an ohmic contact with polyaniline having the value of work function as 4.12 eV. Further, the transfer of an electron from a metal into an insulator requires less energy than its escape to the free space. The height of the potential barrier comprising PEB monolayer is correspondingly reduced when voltage is applied to the metal. Hence, there is a slight displacement of the Fermi level due to tunneling of electrons from silver metal to metal (Ag) through the PEB LB film.[24] Figure 2 shows the I-V characteristics obtained at 20 mV/s for ITO/PEB LB 41 monolayer/Ag (curve I) and In/PEB LB 41 monolayers/Ag (curve 2) devices, respectively. It can be seen that these I-V characteristics are both assymmetric and nonlinear in nature. These devices clearly exhibit rectifying behavior both for forward and reverse bias due to an abrupt increase in current when the potential reaches a value of about 3 V. This result can perhaps be associated with the partial tunneling of electrons through the PEB LB film, whereas the lowering of potential barrier occurs due to the presence of the image force.[25] This is perhaps because the tunneling usually involves the thickness of film lesser than that of the magnitude of barrier height. However, the observed asymmetry in I-V characteristics may be due perhaps to the presence of different molecular states, implying that PEB LB film sandwiched between In and Ag or ITO and Ag could form a basis for the fabrication of molecular rectifiers.[26]

Figure 3 (a) and (b) show the variation of log I as a function of V^n for In/41 layers LB film/Ag and ITO/41 layers LB film/Ag. Simple tunneling at lower voltages can be observed due to the presence of linearity in log 1 versus $V^{1/4}$ plot. Besides this, two different values of slopes in Figure 3 have been observed at higher voltages, indicating once again that simple tunneling is perhaps not predominant at higher voltages in such MIM structures based on ITO and In metal contact electrodes, respectively. The value of n has been found to be 3, indicating the existence of a space charge phenomenon at voltage greater than 1.2 V. This result can perhaps be attributed to the space charge limitation through the medium.

Figure 4 shows the capacitance (C)–voltage (V) plot obtained for Ag/41 PEB LB layers/Ag (curve 1), In/PEB LB layer/Ag (curve 2) and

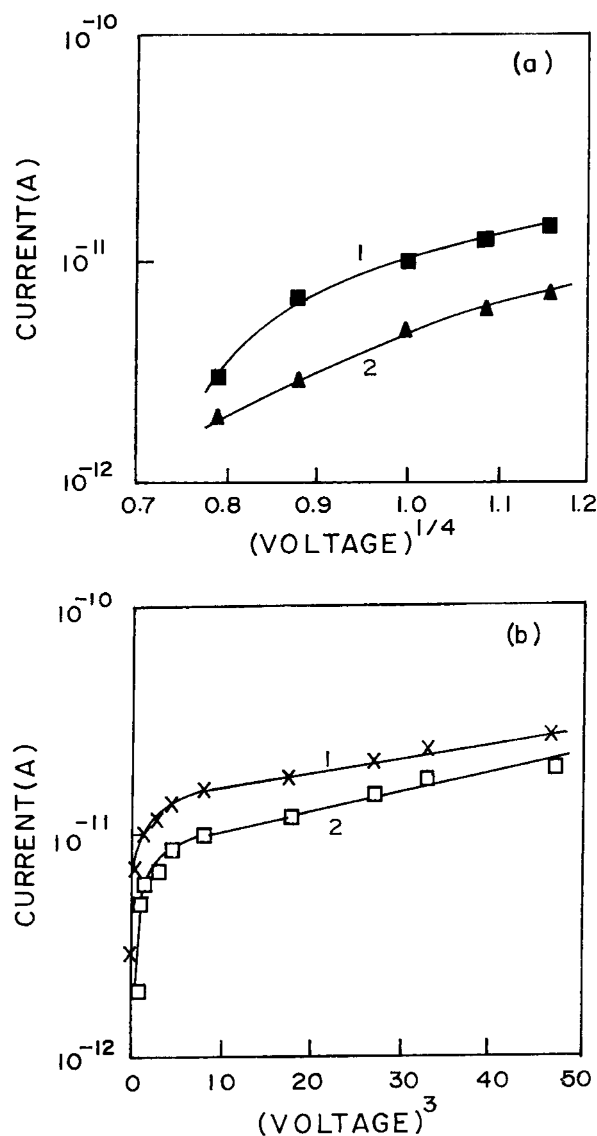

Figure 3 (a) Variation of log current (I) versus $(\text{voltage})^{1/4}$ characteristics (curve 1) for ITO/41 PEB LB films/Ag and (curve 2) for In/41 layers PEB LB films/Ag structures. (b) Variation of log current (I) versus (voltage) characteristics (curve 1) for ITO/41 layers PEB LB films/Ag and (curve 2) for In/41 layers PEB LB film/Ag structures.

ITO/PEB LB layer/Ag (curve 3) structures, respectively. It is interesting to note that in these devices, the capacitance decreases until it reaches 2 V (curve 2 and 3) and reaches the saturation.

Figure 5 (curve 1) shows the variation of capacitance with frequency for Ag/41 PEB LB monolayers/Ag structure. It is seen that capacitance decreases sharply from 0 to 1 V and it remains constant until it reaches 2 V. Besides this, there is a saturation between 3 to 4 V, originating due

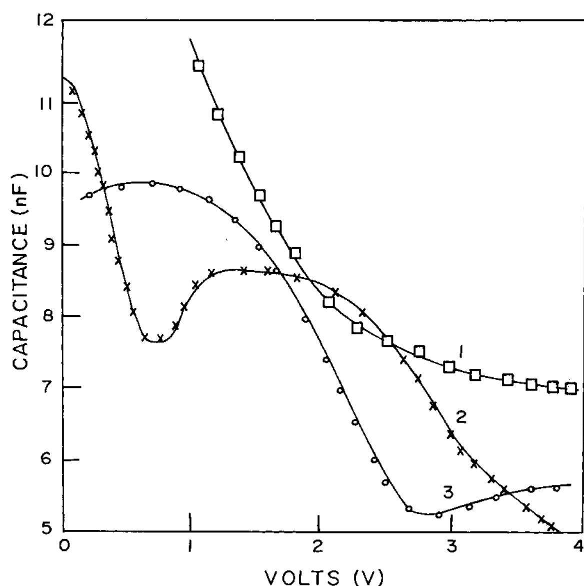

Figure 4 Variation of capacitance (nF) versus voltage (V) of Ag/41 layers of LB PEB film/Ag (curve 1), In/41 layers PEB LB film/LB film/Ag (curve 2), and ITO/41 layers of LB PEB film/Ag (curve 3) structures.

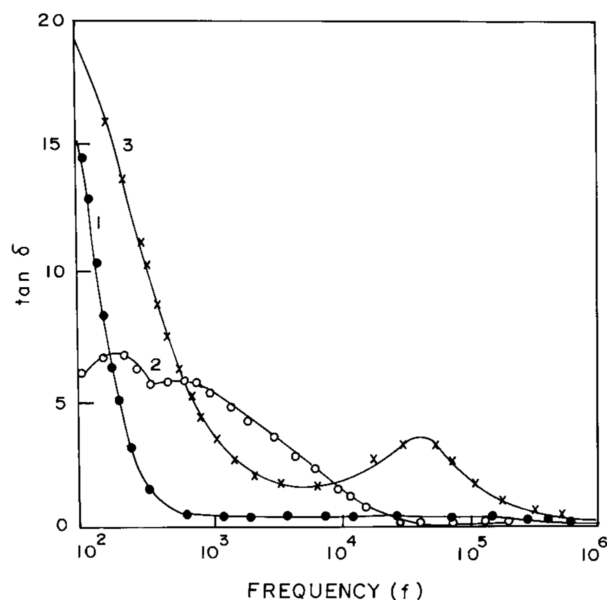

Figure 6 Variation of dielectric loss factor (tan δ) versus frequencies (f) for Ag/41 layers PEB LB film/Ag (curve 1), In/41 layers PEB LB film/Ag (curve 2), and ITO/41 layers PEB LB film/Ag (curve 3) structures.

to the formation of space charges.[25] This form of C-V dependence has been observed for metal/LB/metal structure based on TTF and TCNQ derivatives.[27] Curves 2 and 3 in Figure 5 exhibit the variation of capacitance for In/41 PEB LB layer/Ag and ITO/41 layers PEB LB film/Ag structures, respectively. The observed variation of the capacitance with frequency is in close agreement with the behaviour reported in literature for fatty acids at low polarization arising due to the contact effect. The large dispersion in capacitance at low frequencies can be attributed to the polarization of charges within the interface of the film. The decrease in capacitance at higher frequency ($>10^4$ Hz) results in the onset of polarization of induced dipoles.[28] Such dipoles are perhaps confined at higher frequencies.

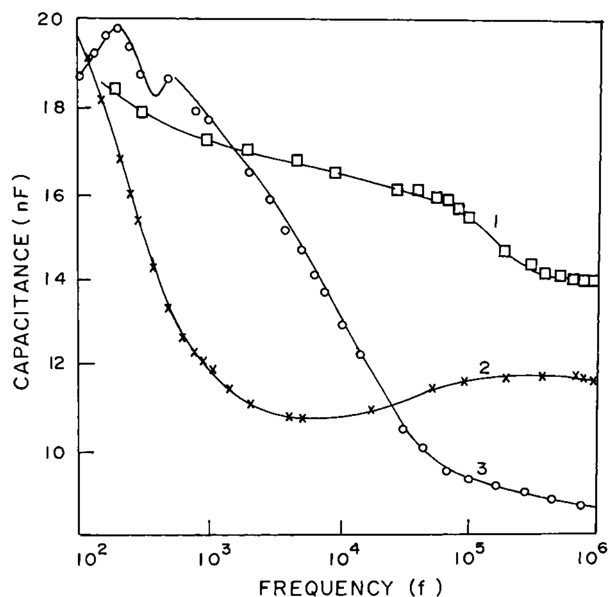

Figure 5 Variation of capacitance (C) versus frequency (f) of Ag/41 layers LB PEB film/Ag (curve 1), In/41 layers PEB LB film/LB film/Ag (curve 2), and ITO/41 layers of LB PEB film/Ag (curve 3) structures.

The alternating current conduction at metal/LB layer/metal junction can be considered to arise as a result of the hopping of charge carriers. At the low biasing condition, capacitance is proportional to w^n, where the value of n lies between 0 and 1.[29] The lower value of both conductivity and capacitance arises due to the presence of Ag electrodes, suggesting that silver perhaps gets oxidized on the LB layers of PEB.

Figure 6 shows the observed variation of dielectric loss (tan δ) obtained for PEB LB layers at various frequencies for Ag/41 layers PEB LB film Ag, In/PEB LB film (41 layers)/Ag, and ITO/PEB LB film (41 layer)/Ag structures, respectively. The low dispersion seen in tan δ versus frequency indicates the absence of inhomogeneity and bar-

rier effect.[30] However, dielectric loss does not follow the usual trend. It is significant to see that ITO/41 PEB LB layers/Ag structures shows the loss peaks at 500 kHz that have also been observed in the case of PANI film.[31]

CONCLUSIONS

The method of fabricating desired MIM devices through PEB LB film sandwiching between metal (Ag/In/ITO) and Ag/PEB LB/Ag structure has been found to exhibit tunneling phenomena, whereas the ITO/PEB LB film/Ag and In/PEB LB film/Ag device shows the space charge-limited current in the insulating PEB LB film. At higher voltages, I versus V^3 dependence for an MIM structure with metal oxide (ITO) and metal (In) indicate rectification behaviour. Further, the Max Wagner polarization has been observed for MIM device with ITO metal. These results show that alternating current conduction in ITO/PEB LB layer/Ag structures is due to the hopping of charge carriers (polarons/bipolarons). However, in order to study the exact mechanism of conduction, it should be interesting to carry out the comparitive studies on temperature dependence of conduction through Langmuir–Blodgett film of polyemeraldine base and poly-n-steroyl-aniline, respectively.

The authors are grateful to Prof. E. S. R. Gopal, National Physical Laboratory, for his constant encouragement and keen interest in this work. We are thankful to Dr. Subash Chandra for many valuable discussions. We thank Dr. S. Annapoorni for interesting discussion during the preparations of the manuscript. M. K. Ram is thankful to CSIR for financial support. Financial support received under Indo-Us fund, project No. DST/INT. VSIF.404/93 is gratefully acknowledged.

REFERENCES

1. N. F. Geddes, J. R. Sambles, D. J. Jarvis, W. G. Parker, and D. J. Sandman, *J. Appl. Phys.,* **71(2),** 753 (1992).
2. H. I. Smith and H. G. Carihead, *Phys. Today,* **43(2),** 24 (1990).
3. M. Schmelzer, B. Burghard, C. M. Fisher, P. Bauerle, H. Scheier, S. Roth, and W. Gopel, *Proceedings of E-MRS Meeting, Symposium D-VII 2,* Strasbourg, 1994, p. 1.
4. F. L. Carter, *Molecular Electronics Devices II,* Dekker, New York, 1987.
5. G. G. Roberts, *Langmuir–Blodgett Films,* Plenum Press, New York, 1990.
6. T. Smimadzu, T. Iyoda, M. Ando, A. Ohatni, T. Kaneto, and K. Honda, *Thin Solid Films,* **160,** 67 (1988).
7. A. T. Royappa and M. F. Rubner, *Langmuir,* **8,** 3168 (1992).
8. K. Hong, R. B. Rosner and M. F. Rubner, *Chem. Mat.,* **2,** 82 (1990).
9. D. Vuillaume, P. Fontaine, J. Collet, D. Dersmes, M. Garet, and F. Rondelez, *Microelect. Eng.,* **22,** 101 (1993).
10. M. K. Ram, S. Annapoorni, and B. D. Malhotra, *J. Appl. Polym. Sci.,* **60,** 407 (1996).
11. D. A. Znameensky, R. G. Yusupov, and B. V. Mislavasky, *Thin Solid Films,* **219,** 215 (1992).
12. M. C. Petty, *Thin Solid Films,* **210/211,** 215 (1992).
13. V. J. Rao and V. S. Kulkarni, *Thin Solid Films,* **168,** 357 (1989).
14. N. J. Geddes, J. R. Sambles, D. J. Jarvis, and W. G. Perker, *Appl. Phys. Lett.,* **56,** 1916 (1990).
15. N. J. Geddes, J. R. Sambles, W. G. Perker, N. G. Couch, and D. J. Jarvis, *J. Phys. D.,* **23,** 95 (1990).
16. M. T. Fowler, M. C. Petty, G. G. Roberts, P. J. Wright, and B. Cockayne, *J. Mol. Electron.,* **1,** 93 (1985).
17. E. G. Wilson, *J. Mol. Electron.,* **7,** 187 (1991).
18. M. K. Ram, N. S. Sundaresan, and B. D. Malhotra, *J. Phys. Chem.,* **97,** 11,580 (1993).
19. R. Kumaran, M. K. Ram, A. S. N. Murthy, and B. D. Malhotra, *Mat. Sci. Eng.,* to appear.
20. N. E. Agbor, M. C. Petty, A. P. Monkman, and H. Harris, *Synth. Metals,* **55–57,** 3789 (1993).
21. M. K. Ram, N. S. Sundaresan, and B. D. Malhotra, *J. Mat. Sci.,* **13,** 1490 (1994).
22. S. C. K. Misra, M. K. Ram, S. S. Pandey, B. D. Malhotra, and Subha Chandra, *Appl. Phys. Lett.,* **61,** 1219 (1992).
23. M. K. Ram, R. Mehrotra, S. S. Pandey, and B. D. Malhotra, *J. Phys. Conden. Mat.,* **6,** 8913 (1994).
24. J. H. Cheung and M. F. Rubner, *Thin Solid Films,* **244,** 990 (1994).
25. C. M. Fischer, M. Burghards, S. Roth, and K. V. Klitzing, *Europhys. Lett.,* **28,** 129 (1994).
26. J. J. Alkena, M. Petty, M. C. Petty, A. S. Dhindsa, J. P. Badyal, and M. R. Bryce. *J. Phys. D.,* **24,** 1422 (1991).
27. M. Sugi, T. Fukui, S. Iizima, and K. Iriyama, *Bull. Electrotech. Lab.,* **44,** 51 (1979).
28. R. Zukeeg, *Solid State Electron.,* **6,** 645 (1963).
29. T. M. Ginnai, D. P. Oxley, and R. G. Pritchard, *Thin Solid Films,* **68,** 241 (1990).
30. A. K. Jonscher, *Phys. Thin Films,* 205 (1980).
31. M. K. Ram, PhD Thesis, Birla Institute of Technology and Science, Pilani, Rajasthan, India, 1995.

Received February 21, 1996
Accepted August 1, 1996