Twenty years of surface science in the Department of Physics, University of Pune

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Surface science has rapidly grown all over the world as a major research area during the last few decades. Physics Department of University of Pune also has established a number of surface techniques. This communication highlights the available techniques in the Department describing briefly some of the interesting work carried out by different groups in the department.

1. Introduction

During the last few decades, rapid development has taken place in order to understand the surfaces and interfaces. A large variety of techniques have been developed[1–3] to determine the surface structure, composition and electronic structure of a wide range of materials even at atomic level. The Physics Department of University of Pune for the last twenty years has attempted to establish a variety of surface spectroscopy and microscopy techniques. In this communication, some of the interesting results obtained using surface techniques by various groups in the department will be described.

2. Experimental techniques

Some of the important techniques established are X-ray Photoelectron Spectroscopy (XPS), Ultra Violet Photoelectron Spectroscopy (UPS), Electron Energy Loss Spectroscopy (ELS), Auger Electron Spectroscopy (AES), Field Emission Microscopy (FEM), Field Ion Microscopy (FIM), Scanning Tunneling Microscopy (STM), etc. Some less conventional techniques like Thermal Desorption (TD) and Thermally Stimulated Exo-electron Emission (TSEE) also have been established. Retarding field techniques, Kelvin probe, field emission/field ion techniques have been utilized to determine either absolute work function or the changes in the work function measurements. Along with these surface sensitive techniques, facilities are developed to *in situ* deposit thin films either by physical vapour deposition or using electron beam. Various groups in the department have developed some specialized facilities like multilayer depositions, laser ablation, chemical vapour deposition, plasma deposition, etc. for *ex situ* depositions. Some of the equipment have been indigenously developed or assembled using commercially available components and modules.

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3. Highlights of research

New materials like diamond-like films, diamond films, fullerenes, polymers, amorphous silicon, high T_c superconductors, quantum dots, magnetoresistive materials, etc. have been synthesized *ex situ* using special instruments. Such new materials developed in the department are usually subjected to surface analysis along with some *in situ* surface or interface analysis. Often some of the materials are subjected to bombardment by high energy electrons, heavy ions, etc. and analysed. Some of the research problems on which substantial work has been carried out in the Department have been outlined, giving a large number of references to assist the interested readers.

3.1. *Metallic glasses*

A number of criteria have been put forth[4,5] to predict the glassy state in alloys which include large atomic size and valence differences among the constituents, near eutectic composition, etc. Attempts were made to establish a correlation between the glassy state and the density of states in the valence band[6,7]. The nearly free electron approach[7] expected a reduction in the density of states in the vicinity of Fermi level. However, the experiments on metallic glasses like Ni-P, NiCrB using XPS showed that this is not always true[8,9]. Metallic glasses containing transition metals have a large density of states near the Fermi level in agreement with the theoretical prediction of Moruzzi *et al.*[6].

Structural correlations in metallic glass[10] and the diffusion of the adatoms in metallic glasses have been investigated using FIM.

3.2. *Semiconductors*

Semiconductor surface and interface investigations form an important research area in the Department.

Interesting investigations on *in situ* deposited Dy, Er, Tm and Ba (precursor to rare earth metals) adatoms on Si(111) were made[11–13] using surface sensitive techniques like XPS, UPS and glancing angle X-ray diffraction (XRD).

Band offset measurements using XPS and UPS on CdS/Si (111) heterojunction have been made by *in situ* deposition of CdS in UHV on cleaned Si (111)-7 × 7 surface[14]. Figure 1 illustrates how starting with clean Si surface heterojunction can be evolved and band offset determined.

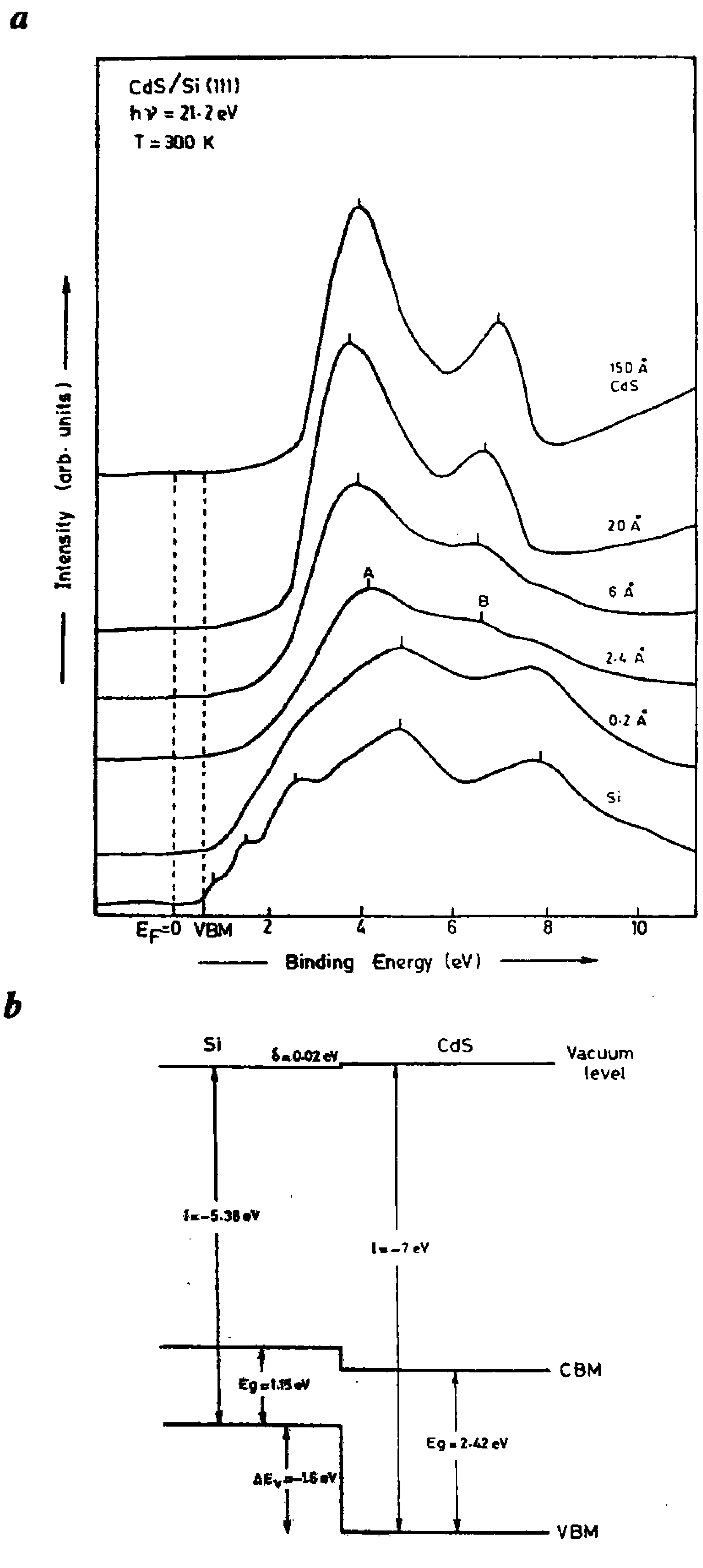

Figure 1. ***a***, **Valence band spectra** of increasing CdS deposition on **Si(111) at 300 K;** ***b***, **Band line-up** diagram constructed using data in **Figure 1** ***a***.

XPS, AFM and photoluminescence have been extensively utilized[15–17] to understand the passivation of GaAs by chemical treatments using Na_2S, $(NH_4)_2S$, NH_4OH, P_2S_5, SeS_2, etc. It was concluded that SeS_2 treatment is the best among many other passivants for GaAs.

Passivating and depinning effects of sulphur-containing polymers and Se-containing thin films have been very effectively identified by the TSEE technique[18]. Native surface states in GaAs and InP have been successfully elucified by TSEE technique[19].

Thin films of amorphous silicon have been investigated quite extensively using both XPS and UPS[20,21]. Field emission technique has also been used[22] to study Stabler–Wronski effect in hydrogenated amorphous silicon coated on tungsten field emitter. The defect states responsible for Stabler–Wronski effect were identified by the TSEE method[23].

Recently films of Ge grown on Si (100) at room temperature have been irradiated with 100 MeV ^{28}Si beam and clustering observed using AFM. XPS analysis of ion irradiated and non-irradiated samples showed that depth profiles in the two cases are quite different which can be attributed to the change in the Ge island density[24,25]. Further work on Ge/Si and In/Si interfaces is under progress. Some work on chemically capped nanoparticles has been published[26] and detailed work is in progress.

Growth and nucleation behaviour of diamond films has been investigated[27–29] using STM. The growth of (100) textured diamond surface was found to exhibit layered growth consisting of pyramid-shaped nanofacets.

3.3. *Metal thin films*

Silver films deposited on silicon substrates at 300°C were investigated using STM with a view of producing atomically flat surface as templates for investigation of adsorbed complex molecules[30]. In another quantitative application of STM the polished surface of polycrystalline silver was investigated[31].

Surface electronic properties of 3d transition metals (Fe, Co, Ni) adsorbates on tungsten single crystal planes have been thoroughly investigated[32–35]. Figure 2 depicts the growth of Ni on tungsten field emitter investigated using FEM. These results also have important contribution towards the understanding of bimetallic catalyst systems used in hydrocarbon industries.

An interesting possibility of synthesis of metastable phases via pulsed laser-induced reactive quenching at liquid solid interface was demonstrated[36,37] in case of H_2O/Fe, NH_3 (liquid)/Fe and C_6H_6/W. Techniques like conversion electron Mössbauer spectroscopy, glancing angle X-ray diffraction, XPS, transmission electron microscopy and Rutherford backscattering spectroscopy were used in the analysis.

Figure 2. Field emission of nickel grown on tungsten field emitter. Highly stable emission is observed.

Recently, work on metallic multilayers has been initiated. Multilayers are analysed[38,39] using glancing angle XRD, XPS and neutron reflectometry in order to investigate interface roughness, composition, electronic structure, etc.

3.4. *High T_c superconductors*

Laser ablation technique has been extensively used in the Department to synthesize high quality thin films of $Y_1Ba_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_8$. Device quality films were developed to produce efficient SQUID and bolometers. Metal and semiconductor films were deposited *in situ* on $Bi_2Sr_2CaCu_2O_8$ high T_c superconductor and interfaces were investigated using photoemission[40–42].

3.5. *Organic thin films*

Organic thin films deposited by plasma polymerization and Langmuir-Blodgett technique have been investigated using XPS and EELS technique to correlate the observed spectral features with the density of states in the conduction band[43,44].

Plasma polymerized methyl methacrylate, methyl styrene films, chlorinated styrene films, etc. were deposited for electron beam lithography application and optimized using XPS analysis[45,46].

Conclusions

In general it can be seen that surface science has flourished in the Physics Department, University of Pune and has helped a lot in understanding the galaxy of new materials also developed in the Department.

1. Briggs, D. and Seah, M. P., *Practical Surface Analysis*, John Wiley & Sons, New York, 1983.
2. Prutton, M., *Surface Physics*, Clarendon Press, Oxford, 1983.
3. Woodruff and Delchar, *Modern Techniques of Surface Science*, Cambridge University Press, 1986.
4. Yavari, A. R., *J. Phys.*, 1986, **F16**, 687.
5. Chen, H. S. and Jackson, K. A., *Treatise on Material Science and Technology* (ed. Herbert, H.), Academic, New York, 1981, vol. 20, pp. 215.
6. Moruzzi, V. L,. Oelhafen, P. and Williams, A. R., *Phys. Rev.*, 1983, **B27**, 7194.
7. Nagel, S. R. and Tauc, J., *Phys. Rev. Lett.*, 1975, **35**, 380.
8. Thube, M. G., Kulkarni, S. K., Huerta, D. and Nigavekar, A. S., *Phys. Rev.*, 1986, **B34**, 6874.
9. Kulkarni, S. K., Thube, M. G. and Nigavekar, A. S., *Phys. Rev.*, 1988, **B37**, 6723.
10. Kanitkar, M. M., Shukla, V. N., Kanitkar, P. L. and Joag, D. S., *Solid State Comm.*, 1984, **50**, 817.
11. Gokhale, S., Ahmed, N., Mahamuni, S., Rao, V. J., Nigavekar, A. S. and Kulkarni, S. K., *Surf. Sci.*, 1989, **210**, 85.
12. Gokhale, S., Mahamuni, S., Deshmukh, S. V., Rao, V. J., Nigavekar, A. S. and Kulkarni, S. K., *Surf. Sci.*, 1990, **237**, 127.
13. Gokhale, S., Mahamuni, S., Joshi, K., Nigavekar, A. S. and Kulkarni, S. K., *Surf. Sci.*, 1991, **257**, 157.
14. Kundu, M., Mahamuni, S., Gokhale, S. and Kulkarni, S. K., *Appl. Surf. Sci.*, 1993, **68**, 95.
15. Kuruvilla, B. A., Ghaisas, S. V., Dutta, A., Banerjee, S. and Kulkarni, S. K., *J. Appl. Phys.*, 1993, **73**, 4384.
16. Kuruvilla, B. A., Dutta, A., Shekhawat, G. S., Sharma, A. K., Vyas, P. D., Gupta, R. P. and Kulkarni, S. K., *Appl. Phys. Lett.*, 1996, **69**, 415.
17. Kuruvilla, B. A., Dutta, A., Shekhawat, G. S., Sharma, A. K., Vyas, P. D., Gupta, R. P. and Kulkarni; S. K., *J. Appl. Phys.*, 1996, **80**, 6274.
18. Bhide, R. S. and Bhoraskar, S. V., *J. Appl. Phys.*, 1992, **72**, 1464.
19. Hullavard, S. S., Bhoraskar, S. V. and Bose, D. N., *J. Appl. Phys.*, 1997, **82**, 5597.
20. Srinivasan, G., Kulkarni, S. K., Bhide, V. G. and Nigavekar, A. S., *Phys. Lett.*, 1989, **A134**, 67.
21. Srinivasan, G., Kulkarni, S. K., Bhide, V. G. and Nigavekar, A. S., *Phys. Lett.*, 1989, **A139**, 338.
22. Joag, D. S., Sharma, A. K, More, M. A., Dusane, R. O. and Takawale, M. G., *Appl. Phys. Lett.*, 1994, **64**, 3437.
23. Bhide, R. S., Manorama, V., Pawar, S. K., Babras, S., Bhoraskar, S. V. and Bhide, V. G., *Appl. Phys. Lett.*, 1990, **57**, 2528.
24. Bhagwat, A., Lobo, A., Sainkar, S. R., Kabiraj, D., Kuri, G. and Kulkarni, S. K., *J. Mat. Sci. Lett.*, 1997, **16**, 1776.
25. Lobo, A., Bhagwat, A. and Kulkarni, S. K., *J. Mat. Sci. Lett.*, 1999, **18**, 453.
26. Kundu, M., Khosravi, A. A., Singh, P. and Kulkarni, S. K., *J. Mat. Sci.*, 1997, **32**, 245.
27. Sumant, A. V., Kshirsagar, R. B., Dharmadhikari, C. V. and Godbole, V. P., *Vacuum*, 1997, **48**, 1005.
28. Sumant, A. V., Dharmadhikari, C. V. and Godbole, V. P., *Mat. Sci. Engg.*, 1996, **B41**, 267.
29. Godbole, V. P., Sumant, A. V., Kshirsagar, R. B. and Dharmadhikari, C. V., *Appl. Phys. Lett.*, 1997, **71**, 2626.
30. Ali, A. O., Kshirsagar, R. B. and Dharmadikari, C. V., *Thin Solid Films*, 1998, **323**, 105.
31. Dharmadhikari, C. V., Kshirsagar, R. B. and Ghaisas, S. V., *Europhys. Lett.*, 1999, **45**, 215.
32. Adsool, A. D., Sharma, R. B., Pandey, R., More, M. A. and Joag, D. S., *Appl. Surf. Sci.*, 1995, **87/88**, 37–44.

33. Sharma, R. B., Adsool, A. D., Pradeep, N. and Joag, D. S., *Appl. Surf. Sci.*, 1996, **94/95**, 177–185.
34. Sharma, R. B., Yawalkar, P. W., Pradeep, N. and Joag, D. S., *Ultramicroscopy*, 1998, **73**, 99–106.
35. Pradeep, N., Sharma, R. B. and Joag, D. S., *Ultramicroscopy*, 1998, **73**.
36. Patil, P. P., Phase, D. M., Kulkarni, S. A., Ghaisas, S. V., Kulkarni, S. K., Kanetkar, S. M., Ogale, S. B. and Bhide, V. G., *Phys. Rev. Lett.*, 1987, **58**, 238.
37. Phase, D. M., Bhandarkar, Y. V., Kulkarni, S. K., Kulkarni, S., Ghaisas, S. V., Kanetkar, S. M., Ogale, S. B., Bhide, V. G. and Guha, S., *Phys. Rev.*, 1987, **B36**, 8237.
38. Vedpathak, M., Basu, S., Gokhale, S. and Kulkarni, S. K., *Thin Solid. Film*, 1998, **335**, 13.
39. Vedpathak, M., Basu, S. and Kulkarni, S. K., *Appl. Surf. Sci.*, 1997, **115**, 311.
40. Kulkarni, P., Mahamuni, S., Chandrachood, M., Mulla, I. S., Nigavekar, A. S., Sinha, A. P. B. and Kulkarni, S. K., *Appl. Phys. Lett.*, 1989, **54**, 2262.
41. Asoka Kumar, P. S., Mahamuni, S., Kulkarni, P., Mulla, I. S., Chandrachood, M., Sinha, A. P. B, Nigavekar, A. S. and Kulkarni, S. K., *J. Appl. Phys.*, 1990, **67**, 3184.
42. Asoka Kumar, P. S., Mahamuni, S., Nigavekar, A. S. and Kulkarni, S. K., *Physica*, 1992, **C201**, 145.
43. Sastri, M., Pal, S., Rajagopal, A., Kundu, M. and Kulkarni, S. K., *J. Chem. Phys.*, 1992, **98**, 1737.
44. Sastri, M., Pal, S., Rajagopal, A., Adhi, S. and Kulkarni, S. K., *J. Chem. Phys.*, 1993, **99**, 4799.
45. Kuruvilla, B. A., Zambre, M., Gosavi, S., Gorwadkar, S., Datta, A., Gangal, S. A. and Kulkarni, S. K., *J. Polym. Sci. Polym. Chem.*, 1994, **32**, 2640.
46. Gosavi, S., Kuruvilla, B. A., Gangal, S. A. and Kulkarni, S. K., *Jpn. J. Appl. Phys.*, 1995, **34**, 630.

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