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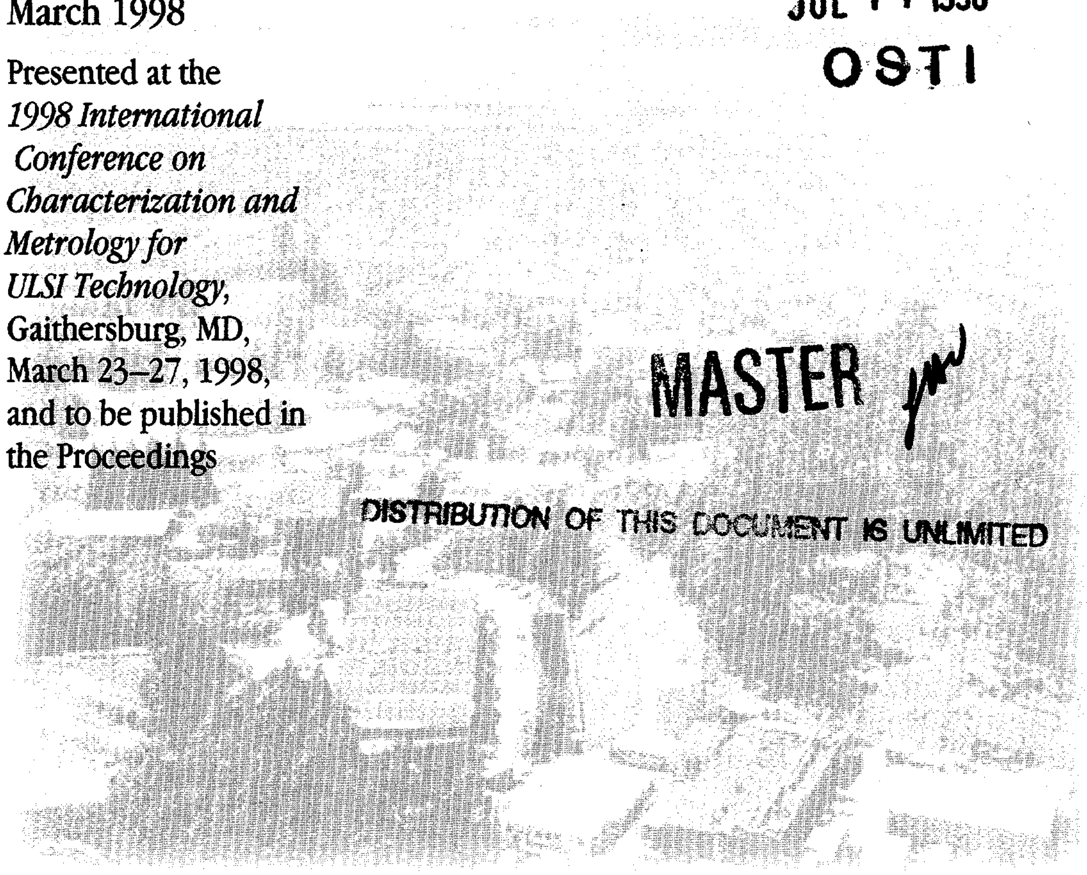

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X-ray photoemission electron microscopy for the study of semiconductor materials

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Photoemission Electron Microscopy (PEEM) using X-rays is a novel combination of two established materials analysis techniques - PEEM using UV light, and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. This combination allows the study of elemental composition and bonding structure of the sample by NEXAFS spectroscopy with a high spatial resolution given by the microscope. A simple, two lens, 10 kV operation voltage PEEM has been used at the Stanford Synchrotron Radiation Laboratory and at the Advanced Light Source (ALS) in Berkeley to study various problems including materials of interest for the semiconductor industry. In the present paper we give a short overview over the method and the instrument which was used, and describe in detail a number of applications. These applications include the study of the different phases of titanium disilicide, various phases of boron nitride, and the analysis of small particles. A brief outlook is given on possible new fields of application of the PEEM technique, and the development of new PEEM instruments.

INTRODUCTION

NEXAFS spectroscopy is an established technique to study materials properties such as elemental composition, bonding structure, and molecular orientation [1]. It is based on the availability of X-ray radiation of tunable wavelength which is produced by a synchrotron. PEEM using X-rays combines NEXAFS properties with high spatial resolution imaging. In addition to topological contrast which is present in a PEEM it is possible to acquire NEXAFS spectra which average over only sub-micron areas, therefore giving elemental and bonding information at with high spatial resolution.

PEEM PRINCIPLE

In an X-PEEM microscope the sample is illuminated by a monochromatized X-ray beam of a diameter larger than the field of view of the instrument. The X-rays are absorbed in the sample and cause photo electron emission which depends on the wavelength of the radiation, the elemental composition, and bonding structure of the elements in the sample. If there is a preferred orientation of molecules in the sample, the X-ray absorption and electron emission also depends on the relative orientation of the molecules and the electrical vector of the radiation for linearly polarized X-rays. A high electric field is applied between the sample and the electron optics to accelerate the electrons, and the electron optics is used to form an image of the emitted electrons. The topological contrast is achieved by the fact that the electric field is distorted at topological surface inhomogeneities which leads to deflection of the electron trajectories. PEEM is a full-field imaging technique and allows therefore real-time imaging of, for example, chemical reactions at surfaces or other time-dependent processes such as annealing phenomena or in-situ film growth. By imaging the sample at incrementally increased X-ray energy it is possible to obtain locally resolved NEXAFS spectra of the sample with an energy resolution given by the resolving power of the synchrotron beamline, and a spatial resolution given by the electron optics column. The highest spatial resolution for a UV PEEM described in the literature is 7 nm [2], and for a PEEM using X-rays 40 nm [3]. The theoretical limit for a PEEM which is corrected for chromatic and spherical aberrations is about 2 nm [4].

EXPERIMENTAL

Figure 1 shows a schematic drawing of the PEEM used for the present experiments. It consist of a system of two electrostatic lenses operating at a nominal voltage of 10 kV. A movable aperture located in the backfocal plane of the objective lens limits the accepted pencil angle of the optics and determines the resolution of the microscope.

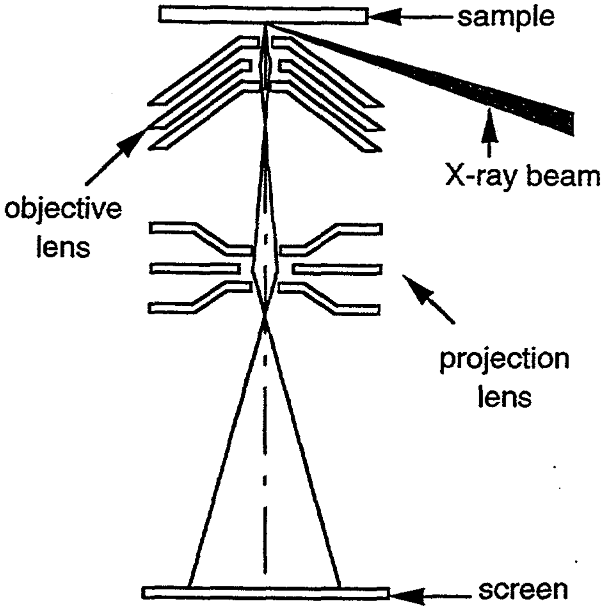

FIGURE 1: Schematic view of a PEEM with two lenses.

The PEEM was used at the Stanford Synchrotron Radiation Laboratory on beamline 10.1 and at the Advanced Light Source in Berkeley at beamline 8.0. The PEEM image is acquired by a microchannel plate, a phosphor screen, and a video camera. The spatial resolution of this microscope is 200 nm limited by vibrations and thermal drift. The sample in a PEEM needs to be conducting to some degree so that charging of the surface does not occur. In cases where this is problem such as, e.g., the study of diamond thin films or ceramic materials, a thin metal (gold or platinum) coating is applied to the surface to avoid surface charging. The probing depth of PEEM is given by the electron escape depth which is about 2-10 nm depending on the material. Due to the elemental specificity of the method, PEEM can study materials buried under a very thin film of another material.

APPLICATIONS

Study of Different Phases of Titanium Disilicide

Titanium disilicide exists in two different phases. One is a metastable C49 base-centered orthorhombic phase with a specific resistivity of 60-90 μΩ, the other one is a stable face-centered orthorhombic C54 phase with a specific resistivity of 12-15 μΩ [5]. The low resistivity phase is desirable for ULSI interconnects, but it has been found that as dimensions shrink the high resistivity phase is formed preferentially [6, 7]. We have studied a titanium disilicide pattern with structures of various dimensions which was deposited on a SiO_2 thin film on a Si wafer. The NEXAFS spectrum of both phases differs at the shoulder of the titanium L3 edge and is the basis for differentiation of the two phases in the PEEM microscope [8]. Fig. 2 shows the titanium L3 edge absorption spectrum for the two phases.

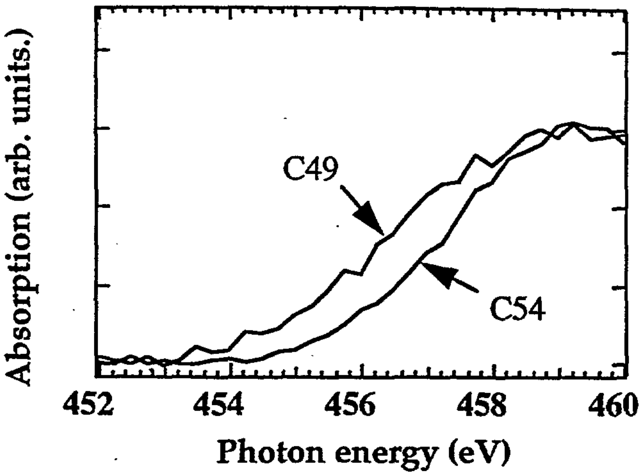

FIGURE 2: Titanium L3 edge absorption spectrum for the two phases of titanium disilicide.

Fig. 3 shows a detail of the patterned structure taken at an X-ray energy below (445.5eV), at the peak (459eV), and at the shoulder of the Ti L3 edge (455eV). Below the edge (Fig. 3a) the titanium pattern appears dark, at the peak (Fig. 3b) the pattern appears bright, whereas at the shoulder of the edge (Fig. 3c) bright edges and bright tips of the spokes are observed indicating a difference in the bonding structure - the formation of the low conductivity phase. As it can be seen in Fig. 2 the low conductivity phase shows stronger absorption at the shoulder of the titanium L_3 edge, therefore the secondary electron emission is higher, and areas of this phase appear brighter in the image. PEEM studies can identify the formation of the different phases of titanium disilicide with high spatial resolution.

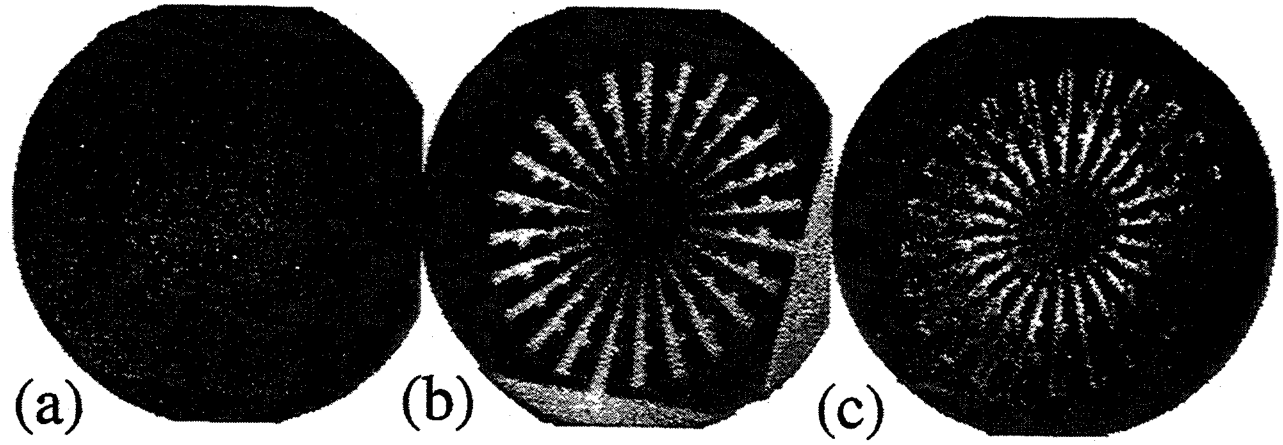

FIGURE 3: PEEM images of the patterned titanium disilicide structure, acquired at an X-ray energy (a) below (445.5 eV), (b) at the peak (459 eV), and (c) at the shoulder (455 eV) of the Ti L_3 edge. The entire spokes pattern is 80 μm in diameter.

Study of Different Phases of Boron Nitride

Boron nitride is an interesting material for technological applications including microelectronic devices, e.g., as gate insulator material on InP [9], and it has been discussed as a candidate for low-dielectric-constant applications [10]. It exists in the sp^2-bonded hexagonal (h-BN), rhombohedral (r-BN), and turbostratic phases, and in the sp^3-bonded cubic (c-BN), and wurtzite (w-BN) phases. NEXAFS is very sensitive to variations in the local bonding structure and therefore is a suitable method to study the various phases of boron nitride [11].

We have investigated BN films which were grown by reactive sputter deposition from a pure boron target on silicon substrates. The samples were locally post-processed by ion bombardment with N_2^+ ions at energies of 90 and 180 keV with total doses of 1×10^{17} cm^{-2}, and with current densities of 80-100 $\mu A\ cm^{-2}$. Fig. 4 shows a PEEM image taken at the π^* resonance of the boron K edge at 192eV. The small wedge is the implanted region.

Figure 5 shows the corresponding local NEXAFS spectra of the implanted and unimplanted region at the boron K edge which were taken by averaging over a region of about 50 μm diameter. Comparison with reference spectra from Jiménez et al. [11] shows that the unimplanted area exhibits a clear hexagonal structure with the boron π^* resonance at 192eV and the σ^* resonance at 197eV. The spectrum is very similar to previously published spectra of films grown by either pulsed-laser or rf sputter deposition [11].

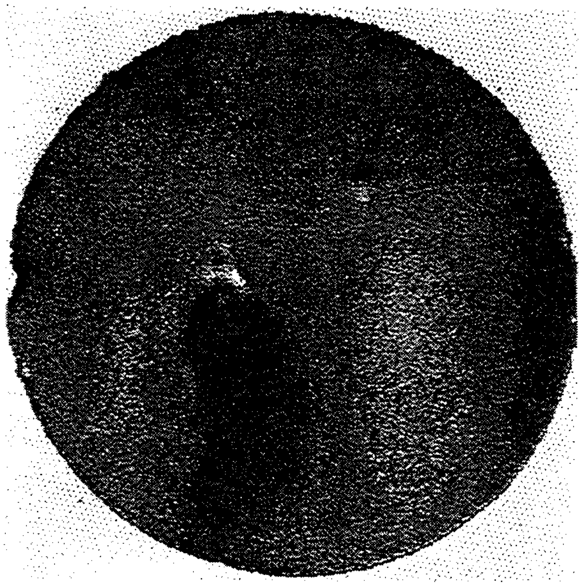

FIGURE 4: PEEM image taken at the π^* resonance of the boron K edge at 192eV. The small wedge is the tip of the implanted region. The field of view is 150 μm.

The small additional features just above the boron π^* resonance are correlated with N-void effects in the hexagonal bonding, i.e. with the fact that boron atoms can be bound to three, two, one, or no nitrogen atoms leading to four different peaks at the π^* resonance. The spectrum in the implanted region exhibits stronger defect features, but no formation of the cubic phase which was observed when films were deposited by ion assisted laser-deposition at lower current densities of 10-70 $\mu A\ cm^{-2}$ [11]. The PEEM image shows that the unimplanted region is brighter than the implanted region due to the fact the boron π^* resonance is stronger for the unimplanted h-BN as shown in Fig. 5. NEXAFS can easily distinguish between the different bonding states of the boron atoms in the thin film and PEEM can show the spatial distribution of the bonding states in the sample as Fig. 4 indicates. PEEM could also be a useful tool for the study of boron bonding states and boron distribution in boron implanted materials.

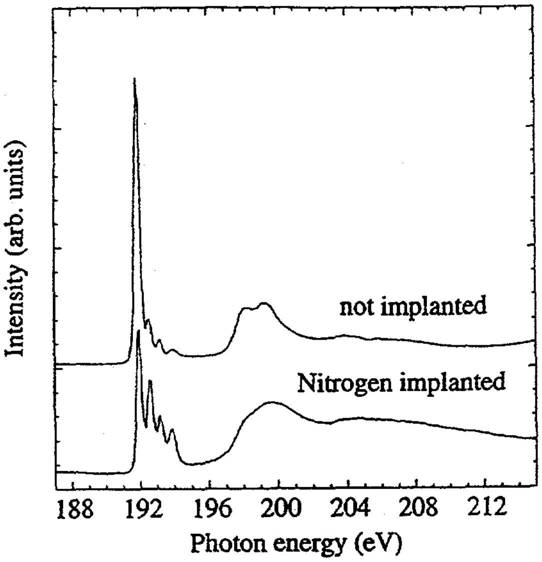

FIGURE 5: Local NEXAFS spectra at the boron K edge taken in the unimplanted and Nitrogen implanted region.

Study of Small Particles

Particle contamination can be a severe problem for semiconductor manufacturing processes, and the identification of the elemental composition and chemical bonding state of small particles can help to identify sources of contamination. PEEM can be applied to the detection and analysis of small particles.

We have studied small particles on diamond-like carbon thin films which were formed by cathodic arc deposition [12]. This material is a promising candidate for a cold electron emitter for flat panel displays. A number of small particles were found at the sample surface after deposition. These particles were several microns in diameter and showed an order of magnitude higher electron emission yield than the surrounding film. The particles were analyzed by taking local NEXAFS spectra on the particle and the surrounding film at the carbon and oxygen K edges. It was found that the particles contained a much higher concentration of oxygen than the surrounding film, and that the oxygen in the particles was bound mainly in carboxyl and carbonate groups. Enhanced field emission which is of crucial interest for flat panel display applications of diamond-like carbon seems to be connected to the enhanced oxygen content of these small particles.

In another experiment we investigated sliders of computer hard disks drives after a wear test which was performed to study the tribological behavior of the disks and sliders [13]. Several small particles were observed at the slider surface after the wear test. Local NEXAFS spectra were taken of these particles and the surrounding slider surface area, and it was found that the particle composition and chemical bonding structure is identical to the amorphous carbon overcoat of the slider surface. This indicates that the particles originate from the slider surface and are not, e.g., dust particles from the environment.

CONCLUSIONS AND OUTLOOK

The combination of NEXAFS and PEEM gives a new tool for the study of materials problems and systems which are of interest to the semiconductor industry. It is possible to analyze the elemental composition and chemical bonding structure of samples with a high spatial resolution. The applications described in this paper are only a small number of possible materials systems which can be studied by this method.

Other materials which are of relevance to the semiconductor industry are polymers, e.g., for photoresist and low-dielectric-constant applications. Systems of polymers have been studied successfully by synchrotron-based X-ray microscopy techniques such as scanning X-ray transmission microscopy (STXM) [14] and PEEM [15]. These methods are particularly sensitive to chemical bonding states in carbon-based materials such as polymers, and can yield comprehensive information about polymer bonding states, spatial distributions of various polymers in blends and multilayers, segregation and dewetting phenomena, polymer degradation, etc.

New PEEM instruments are being build around the world and installed at various synchrotrons. A new instrument (PEEM2) is just being commissioned at the ALS in Berkeley which will be much more user-friendly than existing research-type instruments. It is equipped with an automated, fast sample transfer system, numerous sample preparation and analysis capabilities, in-situ heating and deposition options, and computer control of the electron optics. The availability of new PEEM instruments which are more accessible for users from outside the synchrotron facilities will increase the number of experiments which can be performed and will broaden the fields of applications for these instruments.

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REFERENCES

1. Stöhr, J., *NEXAFS Spectroscopy*, New York: Springer, 1992.
2. Rempfer, G. F., and Griffith, O. H., *Ultramicroscopy* **27**, 273-300 (1989).
3. Bauer, E., Franz, T., Koziol, C., Lilienkamp, G., Schmidt, T., in: Rosei, R. (ed.), *Chemical, Structural, and Electronic Analysis of Heterogeneous Surfaces on the Nanometer Scale*, Kluwer Academic, Dortrecht, in press.
4. Fink, R., Weiss, M. R., Umbach, E., Preikszas, D., Rose, H., Spehr, R., Hartel, P., Engel, W., Degenhardt, R., Wichtendahl, R., Kuhlenbeck, H., Erlebach, W., Ihmann, K., Schlögl, R., Freund, H.-J., Bradshaw, A. M., Lilienkamp, G., Schmidt, Th., Bauer, E., and Brenner, G., *J. Electron Spectrosc. Relat. Phenom.* **84**, 231-250 (1997).
5. Jeon, H., Sukow, C. A., Honeycutt, J. W., Rozgony, G. A., and Nemanich, R. J., *J. Appl. Phys.* **71**, 4269-4276 (1992).
6. Roy, R. A., Clevenger, L. A., Cabral, Jr., C., Saenger, K. L., Brauer, S., Jordan-Sweet, J., Buccignano, J., Stephenson, G. B., Morales, G., and Ludwig, Jr., K. F., *Appl. Phys. Lett.* **66**, 1732-1734 (1995).
7. Saenger, K. L., Cabral, Jr., C., Clevenger, L. A., Roy, R. A., and Wind, S., *J. Appl. Phys.* **78**, 7040-7044 (1995).
8. Singh, S., Solak, H., Krasnoperov, N., Cerrina, F., Cossy, A., Díaz, J., Stöhr, J., and Samant, M., *Appl. Phys. Lett.* **71**, 55-57 (1997).
9. Paul, T. K., Bhattacharya, P., and Bose, D. N., *Appl. Phys. Lett.* **56**, 2648-2650 (1990).
10. Maeda, M., Jap. J. Appl. Phys. **29**, 1789-1794 (1990).
11. I. Jiménez, A. F. Jankowski, L. J. Terminello, D. G. J. Sutherland, J. A. Carlisle, G. L. Doll, Tong, W. M., Shuh, D. K., and Himpsel, F. J., *Phys. Rev. B* **55**, 12025-12037 (1997).
12. Díaz, J., Anders, S., Cossy-Favre, A., Samant, M., and Stöhr, J., *Appl. Phys. Lett.*, submitted for publication
13. Anders, S., Stammler, T., Bhatia, C. S., Stöhr, J., Fong, W., and Bogy, D. B., *Spring Meeting of the Material Research Society*, San Francisco, 1998, to be published
14. Winesett, D. A., Ade, H., Smith, A. P., Rafailovich, M., Sokolov,S., and Slep, D., *Microscopy and Microanalysis*, to be published (1998).
15. Anders, S., Stammler, T., Ade, H., Slep, D., Sokolov, J., Rafailovich, M., Heske, C., and Stöhr, J., *1997 Compedium of the Advanced Light Source*, Berkeley, to be published