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Positron Annihilation Spectroscopy: A Review of Applications in Nanomaterials Thin films and Semiconductors

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ABSTRACT: A brief review have been presented highlighting the use of positron annihilation spectroscopic techniques for exploring the physical properties of materials from bulk to nanocrystalline sized particles. Even though a direct correlation of the changed annihilation characteristics with predictable changes in the solid is certainly not possible, positron annihilation can be used for obtaining complementary evidences to substantiate such predictions. Different types of materials exhibiting different types of transitions have been investigated and the results powerfully portray the sensitivity of positrons to changes in the electron density and momentum distributions in the annihilation sites. Measurements of positron lifetimes and the line shape parameters of the Doppler broadened gamma ray spectra are carried out as functions of either mean grain sizes or temperature and from the variations of these quantities, defect-specific information are extracted, which are then interpreted in terms of the atomic rearrangement within the solid. PAS is a novel technique which uses the positron as capable of probing the atomic and molecular scale (0.2-2 nm) free-volume, interfaces, nanovoids, thermal vacanices and hole properties in polymeric, nanocomposites and semiconductor materials. This paper presents applications of PAS to determine positron lifetime in nanoparticles, thin films and glass transition temperatures in polymers.

Keywords: Positron Annihilation Spectroscopy, Thin Films, Nanocrystalline Materials

I. INTRODUCTION

Researchers in many scientific areas and applications are focusing on ever smaller and smaller dimensions and therefore searching appropriate investigative methods. Nuclear methods have proved themselves as especially useful, and among them positron annihilation spectroscopy (PAS) has been playing eminent role since the beginning of its exploitation several decades ago, and still presents very vigorous field of research ++. PAS has been used to study defects in solids for many decades [1]. The characteristics of annihilation photons contain electronic properties when the positron encounters electrons Fig.[1] and it annihilates into γ-rays by $E = mc^2$, i.e. wave function, density, and energy levels of matter at the location where the positron annihilates [1,2]. Recently it has been successfully applied to chemical systems [2] to measure the free volume properties in polymers and in biological systems [3]. With its unique sensitivity to the atomic-level free volume in polymers, it is promising tool to measure free-volume properties as a function of depth when one employs a variable mono-energy positron beam [4-6]. Positron annihilation lifetime (PAL) spectroscopy [2] is capable of determining size, quantity, distribution, and relative fraction of free volume in polymers due to the fact that the ortho-Positronium (oPs, the triplet Positronium) is preferentially trapped in the sub nanoscale free volume. Similarly, Doppler broadening energy spectroscopy (DBES) [2] is another efficient technique to probe para-positronium (p-Ps, singlet Positronium) and chemical composition of chemical and biological systems. The principles of positron annihilation in condensed materials can be successfully utilized to explore several interesting aspects of materials.

II. EXPERIMENTAL TECHNIQUES

There are three main techniques of positron annihilation spectroscopy which can be used both with the positrons from sources and slow positron beams: (1) positron annihilation lifetime spectroscopy (PALS), (2) Doppler broadening spectroscopy and (3) angular correlations measurements. The principles of these techniques are illustrated in Fig. 1.

III. POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

In the positron annihilation lifetime spectroscopy, when used with radioactive sources, ^{22}Na is usually used as positron source. In this case PALS is based on the measurements of the time difference between 1.274 MeV γ- ray, emitted from the daughter ^{22}Ne nucleus almost immediately after positron emission from the ^{22}Na, and one of the annihilated 0.511 MeV γ-rays emitted in positron annihilation. The collected time spectra contain various lifetime contributions and decomposition in individual time components and corresponding intensities can yield information about holes in the sample and their concentrations. This technique, when used with slow positron beam, should include some gating from the incoming positrons in beam, but with the definite positron energy, the exact penetration depth can be determined. In addition to the changes in the electron momentum distribution, a trapped positron also experiences a decrease in electron density, which is accompanied by a corresponding increase in lifetime. In PALS one measures the distribution of positron lifetimes and their intensities. In classic PALS setups, the timing start signal is provided by a gamma-ray that is released coincidentally from a radioactive source with the positron. The stop signal is one of the annihilation gamma-rays. Two phototubes are used to detect the start and stop gamma-rays [7]. The advantages of this type of PALS is a high count rate and a relatively simple experimental apparatus. This disadvantage is that the positrons are implanted very deeply and in an uncontrolled fashion so that only *average* properties of the sample can be studied with positrons.

The major advantage of beam PALS is the ability to control positron implantation. Samples can be depth-profiled by varying the incident beam energy. This technique has been used to determine the free-volume hole size distributions in various polymers as a function of temperature, pressure, and physical aging. It is a relatively new technique, which holds great promise, particularly in the study of porous films, such as low-k thin films.

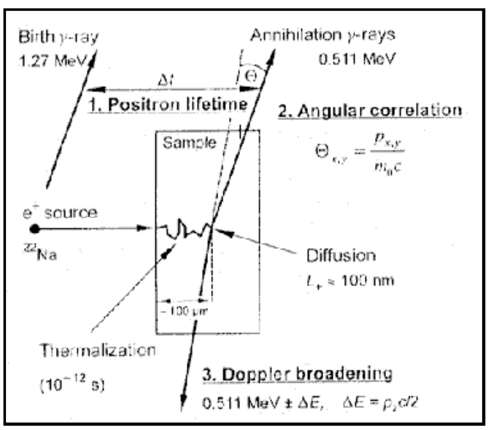

Fig. 1.

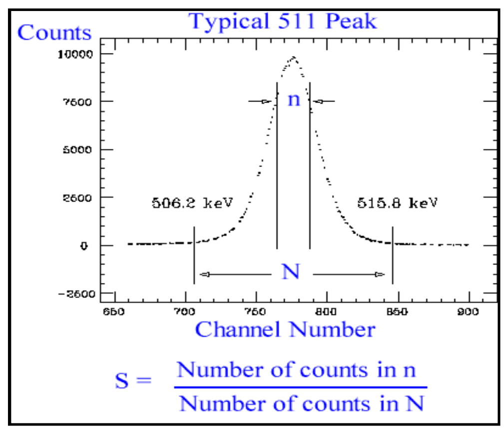

Fig. 2.

IV. DOPPLER BROADENING SPECTROSCOPY

In Doppler broadening spectroscopy the precision measurement of energy shift of the annihilated 0.511 MeV γ-ray as a consequence of non-zero momentum of annihilated positron and electron pairs is used to extract information about electron distributions in the investigate sample. One can detect either only one annihilated gamma ray (single Doppler broadening spectroscopy) or, in order to reduce the background, coincidence between the two outgoing 0.511 MeV γ-rays can be used (coincidence Doppler broadening spectroscopy). This non-zero momentum of annihilated positron-electron pairs causes also deviation from co-linearity of the two outgoing γ-rays, and these angular deviations can be registered in γ- γ coincidence measurements in one or two dimensions, and form basis of angular correlation measurements Fig.2. But to achieve required angular resolution in these measurements gamma ray detectors should be several meters apart and require special laboratory arrangements. Positrons trapped in defects have a smaller probability of annihilating with deeply bound core electrons and a larger probability of annihilating with lower momenta valence electrons. This results in a smaller average energy shift. Thus, defects tend to narrow the experimental line width. In DBS one generally characterizes the width of the energy distribution by the *sharpness* or S-parameter.

V. POSITRON MICROSCOPY

The first type of positron microscopes is analogous to the transmission electron microscope (TEM) and is called the transmission positron microscope where positrons passing through a thin sample are focused on a channel electron multiplier array (CEMA), and the resulting magnified image is accumulated by a computer. Since this technique cannot readily make use of any of the unique positron characteristics discussed above, it propose only a few potential advantages over a TEM.

Shortly thereafter, however, a much more useful type of direct imaging microscope called the positron reemission microscope (PRM) was reported, which does exploit unique positron characteristics Fig.[3]. In the PRM (shown schematically in the figure on the right), positrons are implanted in a thick sample and allowed to thermalize and diffuse. Those that reach the surface are reemitted are then accelerated, magnified, and focused on a CEMA to form an image. Thus the imaged signal is related to the number of particles reemitted, a signal which is unique to positrons.

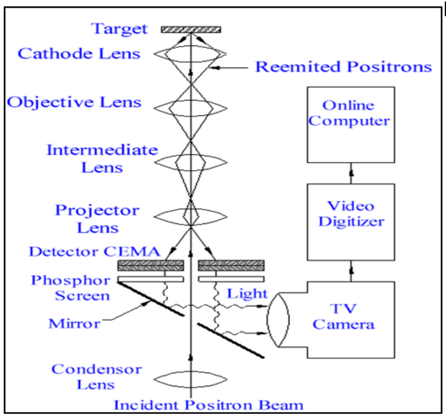

Fig. 3.

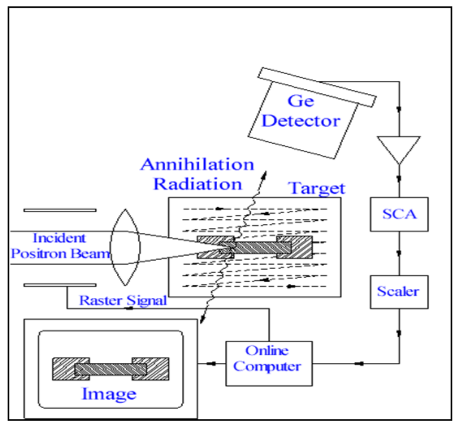

Fig. 4.

The PRM offers potential resolutions below 10 angstroms, and should be particularly useful in studies of surfaces and thin over layers, as well as in biological applications. Any process in the solid that either enhances or suppresses the probability of positron reemission from a particular point on the target surface can be a contrast mechanism for this microscope. Defect trapping, work function changes, surface trapping, positronium formation, and other positron interaction mechanisms can thus be imaged. The reemission probability can be a very sensitive measure of surface conditions in some cases. It may be possible to image over layers having thicknesses of only 1-2 monolayers, and thus to observe such phenomena as islanding or adsorbate segregation. Depth profiling using the PRM may be feasible, but the actual depth from which information can be obtained is limited by the requirement that positrons be able to reach the surface and be reemitted in order to be imaged. This limits the depth to which the beam positrons can be usefully implanted to roughly a diffusion length (100-1000 angstroms) depending on sample conditions).

The third type of positron microscope, analagous to the scanning electron microscope, is called the scanning positron microscope (SPM). In the SPM Fig.[4] a beam of positrons of microscopic diameter is rastered across a surface, and a positron-related signal is recorded synchronously. An image is built up in a computer by recording the amplitude of the signal at each point in the raster. The signal can be any of the unique positron signals, for example, reemitted positron rate, energy of the reemitted positrons, positronium fraction, annihilation gamma-ray energy or angle, or positron lifetime. The advantages of the SPM are the wide variety of signals available and the ability to examine target properties at various depths from the surface. The disadvantages of the SPM are the fact that ultimate resolution is limited by the diffusion spreading of positrons in the incident beam spot to roughly a diffusion length (100-1000 angstroms) as mentioned above), and the need for more intense beams to provide sufficient rate to produce full two-dimensional images.

VII. CONCLUSIONS AND ITS APPLICATION

If we consider about positron annihilation from the general point of view, we could say that the positron annihilation spectroscopy (PAS) is nowadays well recognized as: - a powerful tool of microstructure investigations of condensed matter as show by diagram in Fig. [5].

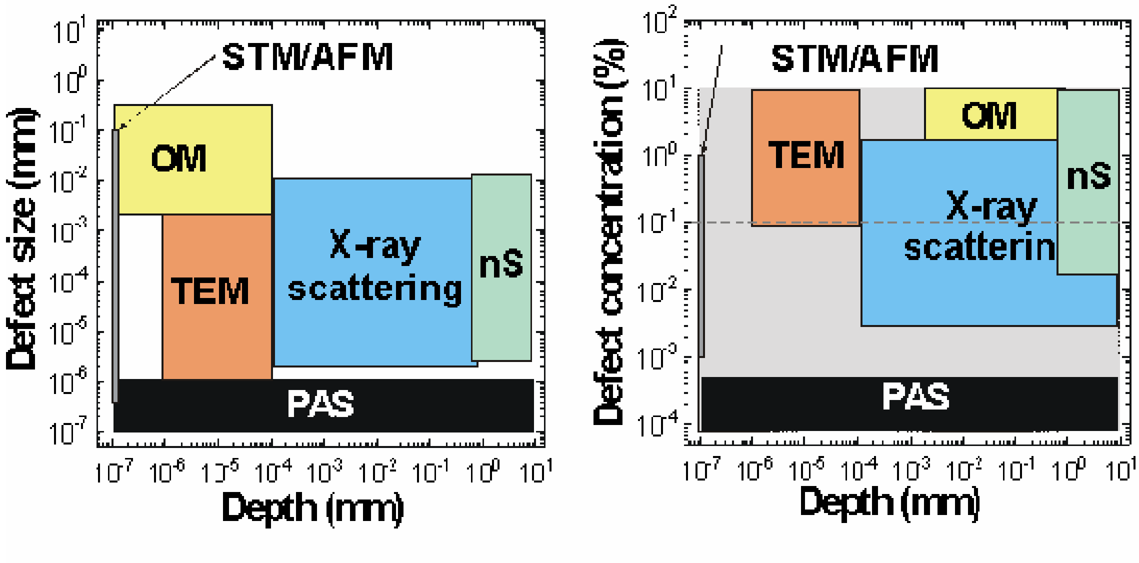

Fig. 5. General overview of applicability range for some spectroscopy techniques.

Where (OM – optical microscopy, TEM - transmission electron microscopy, nS – neutron scattering, STM/AFM – scanning tunnelling microscopy/atom probe ion microscopy). Positron Annihilation Lifetime Spectroscopy (PALS) has tremendous potential as a powerful tool for quantifying the types and densities of defects in solids. PAS is a unique tool for studying nanoscopic open-volume defects, such as vacancies, vacancy clusters, dislocations, nanoprecipitates, nano-porosity, grain boundaries of nano-grains, acceptors (in semiconductors) defect type and density may be determined. The other outstanding field of application of positron annihilation detection is medical imaging [8]. Positron annihilation is used in various imaging systems such as gamma camera, sPECT, PET, CT-PET, etc. Investigations of semiconductors was one of the most active fields of research in material research, and they have been followed the initial investigations of metals and alloys. When positrons diffuse through some crystal, they can be captured in trapping sites produced by crystal imperfections e.g. vacancies and dislocations. This changes positron lifetime in the crystal, and the measured positron lifetimes can be correlated with structural imperfections and their concentrations. In porous materials beside direct positron annihilation, if available space permits, a formation of positronium can be possible. Positronium formation and their lifetimes in voids can give information about the sizes and distributions of the voids in the investigated samples. There are also possible medical and biological applications such as e.g. for regeneration of artificial dialysis solution, in administration of contrast agents in magnetic resonance diagnosis, for protein binder and carrier, as well as carrier for vitamins, minerals or toxic compounds, etc. Of course, also many other fields of research have been very successfully exploited these techniques,

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