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Positronium annihilation in silica aerogel studied by a positron age-momentum correlation technique*

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Abstract A high-performance positron age-momentum correlation (AMOC) spectrometer was newly developed. The counting rate is increased up to 200 cps much larger than the value 20 cps reported by other international groups. And at the same time, the time resolution still keeps at the international level of 220 ps. Furthermore, positronium (Ps) annihilation in silica aerogel was investigated by AMOC, which indicates: (1) Ps annihilation between the grains dominantly undergoes pick-off process and spin conversion from o-Ps to p-Ps; (2) Annealing below 400 ℃ changes the grain surface conditions, i. e. the desorption of hydrogen and the decrease of the defect centers concentration.

Key words positron age-momentum correlation, positronium formation, positron states, silica aerogel

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1 Introduction

Positron annihilation spectroscopy is sensitive to atomic defects and as a nondestructive probe has been successfully used to study electronic structure, micro-structural defects, surface properties, chemical reactions, etc[1]. All information is represented by different positron states. For materials with high electron density, such as metals and semiconductors, free annihilation in crystal lattice and trapped annihilation in vacancy-type defects can be observed and the positron lifetime from such states is ranged from 0.2 to 0.4 ns[2]. And for other materials with lower electron density, such as polymers and porous materials, positrons can capture an electron to form either p-Ps (para-positronium) or o-Ps (ortho-positronium), in the ratio 1:3. The decay of Ps in condensed matter proceeds either through self-annihilation as a p-Ps into two γ rays in some 0.125 ns, or as an o-Ps into three γ rays in $\sim$140 ns. The overlap between the o-Ps wave function and the electron wave function of the medium gives rise to electron pick-off where the positron, bound to an electron in an ortho state, annihilates in fast para-annihilation with a foreign electron of the environment. Electron pick-off reduces the o-Ps lifetime to 1—100 ns and the lifetime directly reflects the size of annihilation environment, such as free volumes and pores, corresponding Doppler broadening of energy spectrum related to the conditions of grain surfaces and pore walls[2—4]. Furthermore, some paramagnetic gases (oxygen) or defect centers carrying unpaired electrons even convert o-Ps into p-Ps and at the same time narrow the Doppler broadening spectrum[5]. Therefore it is significant to distinguish the different positron states in age domain and thus to thoroughly investigate the micro-structural defects and the chemical surroundings on the pore walls and in the grains for porous materials, ultra-fine powders.

Conventional positron methods, present a linear sum of the information from different annihilation states[6], however, positron age-momentum correlation technique (AMOC) covers this shortage by time-selected energy spectrum. AMOC has been demonstrated as a potential tool to examine the chemical modification of pore walls in porous materials, the mechanism of Ps formation and annihilation, chemical reactions of Ps[7]. But limited to some factors,

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such as multi-parameter coincidence acquisition, this technique is developed slowly and there is no practical spectrometer at present except for Germany[8] and Japan[3]. In the present work, an newly developed AMOC instrument is introduced in detail and the behavior of Ps annihilation in silica aerogel (an aggregate of α-SiO_2 ultra-fine grains) as well as the low-temperature annealing effect is also discussed in terms of the grain surface conditions.

2 Experimental setup and performance testing

Figure 1 shows the block diagram of the AMOC system. The positron source, 50 μCi of ^{22}Na, is sandwiched between two identical samples. The whole system can be divided into three parts: positron lifetime measurement consisting of fast scintillation detectors $D_{1,2}$, CFDD and TAC, Doppler broadening of energy spectrum including HPGe detector and amplifier, and other NIM modules belonging to the time coincidence unit. The lifetime spectroscopy part of this system uses the γ-γ timing, and the detectors D_1, D_2 are respectively used to detect 1.28 MeV γ rays as a starting signal and the annihilated ~0.511 MeV γ rays as a stop signal. The coincidence unit is used to strobe DADC only when valid events occur, i. e. 1.28 MeV and two annihilated 0.511 MeV γ rays are detected simultaneously by three detectors. Then the data received by DADC will be transferred to computer by USB. By time coincidence, the high-energy background from pile-up signals and the Compton scattering of 1.28 MeV γ rays in conventional Doppler broadening measurement, can be reduced to a certain extent. Our experiments demonstrate that it is feasible to adopt a fast-slow coincidence mode because of poor time-resolution of HPGe detector. The so-called "fast" means that the time interval between two signals from lifetime part is not more than 100 ns and the so-called "slow" means that the interval between fast-coincidence output and energy signal is ~ μs. The fast-slow coincidence technique effectively increases the coincidence count rate up to 200 cps satisfying measurement need of $>10^7$ counts per day while the values reported by other international groups are not more than 20 cps. "DADC" in Fig. 1, denotes a fast parallel multi-channel data acquisition system based on FPGA designed in our lab and the details of this system were described in our patent[9]. A 2 mm thick Pb plate was placed between the source and detector to absorb small energy photons reducing the effect of pile-up[3].

Furthermore the data received by computer are not saved directly but still analyzed and filtered by special algorithm software. Such events, in which the amplitude of energy signal (the output of Amplifier) is far from 0.511 MeV or the width is far beyond the normal value (such as 6 μs in 2 μs shaping time), will be rejected. This method can decrease the background of spectra by an order of magnitude.

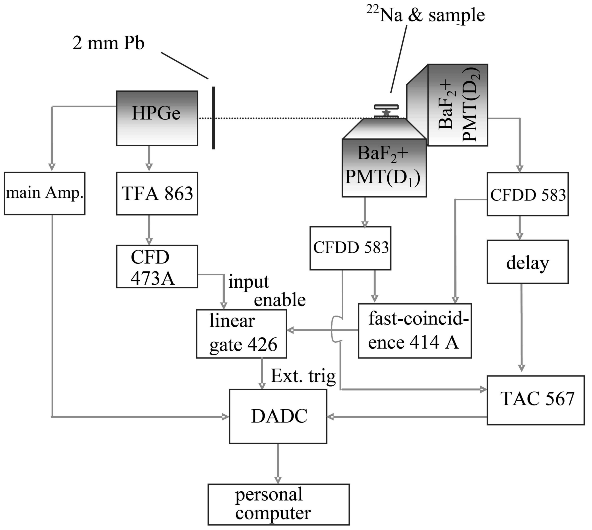

Fig. 1. Block diagram of the triple-coincidence AMOC system. (DADC: multi-channel data acquisition system equipped with analogue-to-digital converter and coincidence unit).

For the present source-based AMOC spectrometer, the energy resolution is 1.2 keV (FWHM, measured at 514 keV from ^{85}Sr) and the time resolution still keeps at the international level of 220 ps (Fig. 2) at the coincidence count rate of 200 cps. Fig. 3 shows a three-dimensional AMOC relief (number of counts vs. positron age and energy of the positron annihilation γ rays) of silica aerogel measured at room temperature under N_2 protection. The positron lifetime spectrum can be obtained by integrating the AMOC spectrum along the energy axis (Fig. 4(a)) and similarly the Doppler broadening spectrum by integrating the AMOC spectrum along the age axis (Fig. 4(b)).

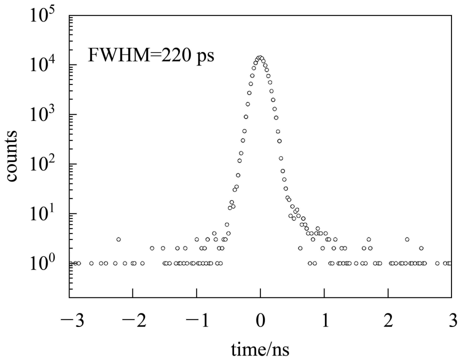

Fig. 2. Time resolution spectrum measured with ^{60}Co.

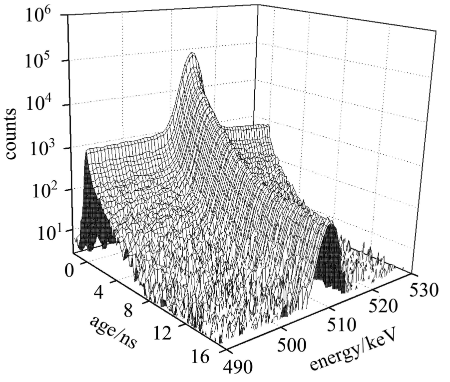

Fig. 3. AMOC relief of silica aerogel measured at room temperature under N_2 protection.

3 Observation of positronium annihilation in silica aerogel and discussion

The momentum distribution of the annihilating positron-electron pairs is characterized by the age-dependent lineshape parameter $S^t(t)$, where t denotes the positron age. In analogy to the integral lineshape parameter, $S^t(t)$ is defined by the number of counts in a central region of the Doppler-broadened 0.511 MeV line normalized by the total number of counts[8]. Low $S^t(t)$ values correspond to strong Doppler broadening and thus to a wide momentum distribution.

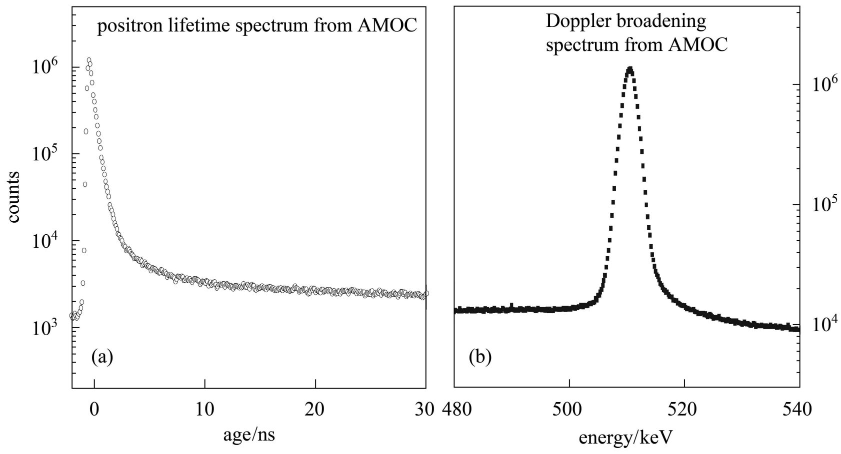

Fig. 4. Integrated lifetime and Doppler broadening spectrums from AMOC relief.

Figure 5 shows the $S^t(t)$ curves of three representative samples, polymer, silica aerogel and defect-free silicon. The large S^t parameter values below 0.5 ns indicate that in polymer and silica aerogel Ps was formed, in contrast to defect-free silicon, in which "young" e^+ do not show particularly large S^t values and where Ps should indeed not form. That is because the narrow components of the 0.511 MeV lines responsible for the large S^t values are due to p-Ps with a mean lifetime of about 0.125 ns. At larger ages around 1.5 ns, the $S^t(t)$ parameter is dominated by the annihilation of "free" positrons and by the pick-off annihilation of o-Ps in the free volumes of polymers and the grains of silica aerogel. The unchanged S^tvalues at around 4 ns for polymer indicate the pick-off process in free volumes while the larger values at around 10 ns for silica aerogel indicate the annihilation process of Ps between the grains. For silicon, the $S^t(t)$ curve almost remains a horizontal line due to an absence of Ps in such compact materials. The different annihilation behavior of positrons in three representative samples is obviously described, which demonstrates the measurement reliability and stability of this spectrometer.

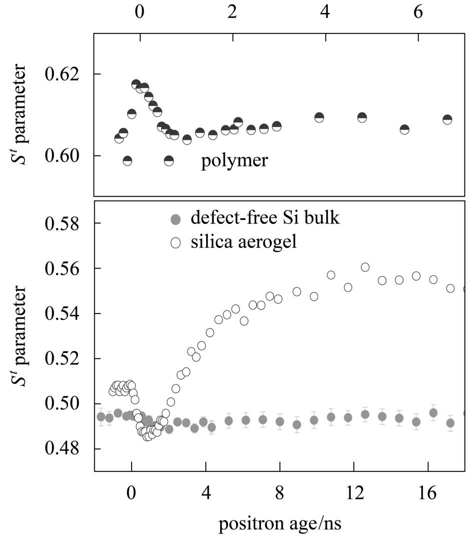

Fig. 5. Lineshape parameter S^t versus positron age of representative samples polymer, silica aerogel and defect-free silicon.

Figure 6 shows the $S^t(t)$ curves of untreated, annealed at 150 ℃ and 300 ℃ silica aerogel for 2 h under high vacuum (10^{-5} Pa). A much larger S^t value at around 10 ns, than those of p-Ps annihilation and

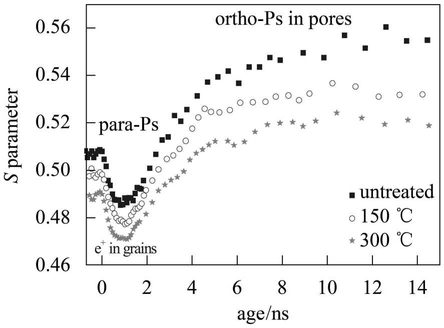

Fig. 6. Lineshape parameter S^t versus positron age of silica aerogel annealed at low temperatures.

pick-off process in the grains, makes clear that the o-Ps annihilation between the grains dominantly undergoes pick-off process and the spin conversion from o-Ps to p-Ps (o-p conversion)[10]. After annealing, a uniform decrease of S^t values at 10 ns was found which should be considered as the reduction of Ps formation probability and o-p conversion probability caused by the change of grain surface conditions. On the one hand, it is known that desorption of hydrogen from dihydride species (such as H_2O) of the grain surface occurs in the range $\sim$200 ℃, and hydrogen is considered to be an impurity which decreases the activation energy of Ps formation[1]. On the other hand, the concentration of various kinds of defects such as dangling bonds, E' centers, non-bridging oxygen hole centers and other defects on the grain surface, may be reduced after annealing. Such defects with unpaired electrons are candidates for Ps spin-conversion[11].

4 Conclusions

By a fast-slow time coincidence technique, a high-performance AMOC spectrometer was developed in our lab with high coincidence count rate (200 cps) and time resolution (220 ps). And an effective algorithm for rejecting the pile-up signals can decrease the background of spectra by an order of magnitude. The characteristic annihilation behaviors of positron in representative samples (polymer, silica aerogel and defect-free silicon), have been observed, demonstrating the reliability of this instrument and high sensitivity to different defect configurations.

The study of Ps annihilation in silica aerogel, illustrates: (1) Ps annihilation between the grains dominantly undergoes the pick-off process and the o-p conversion; (2) Annealing below 400 ℃ changes the grain surface conditions, i. e. the desorption of hydrogen and the decrease of the defect centers concentration.

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