Identification of Deep Defects by Positron Annihilation Spectroscopy in Annealed GaAs Thin Films

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□ ABSTRACT □

Positron annihilation spectroscopy was applied to investigate the defect properties in GaAs thin films at different annealing temperature. Positron lifetime and Doppler broadening spectroscopy using mono-energetic positron beam were used to identify the defects in the GaAs films. Theoretical calculations of the positron lifetime were performed. DBS measurements showed, that with increasing the annealing temperature increases the deep defect density. Lifetime measurements confirmed this result. The decomposition of the lifetime spectra of the samples resulted in the detection of two vacancy-related defects: a vacancy $3V_{Ga}$ or $3V_{As}$ (annealing temperature is less than 650 K) and a negatively charged vacancy complex $(V_{Ga} - V_{As})^{-}$ (annealing temperature is more than 650 K). Furthermore, Lifetime measurements interpreted the presence of large cluster of vacancies by the near-surface defective regions.

Keywords: Positron annihilation spectroscopy, Defect, Vacancy, Doppler broadening, Lifetime of positron, Annealing.

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تحديد العيوب البلورية المتشكلة في عينات ملدّنة من زرنيخ الغاليوم بواسطة مطياف فناء البوزيترونات

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□ ملخّص □

تم تطبيق التحليل الطيفي لإفناء البوزيترون لفحص خواص العيوب في الأفلام الرقيقة المصنوعة من زرنيخ الغاليوم (GaAs) عند درجات حرارة تلدين مختلفة. تم استخدام عمر البوزيترون والتحليل الطيفي لتوسّع دوبلر (DBS) باستخدام شعاع البوزيترون أحادي الطاقة لتحديد العيوب المتشكلة في الأفلام الرقيقة GaAs. تم إجراء الحسابات النظرية لعمر البوزيترون. أظهرت قياسات DBS أنه مع زيادة درجة حرارة التلدين تزداد كثافة العيوب البلورية العميقة (تركيز العيوب البلورية). أكدت قياسات عمر البوزيترون هذه النتيجة. أدى تحليل الطيف المتعلق بعمر البوزيترونات إلى اكتشاف نوعين من العيوب المرتبطة بالفجوات: الفجوات $3V_{Ga}$ أو $3V_{As}$ (عندما تكون درجة حرارة التلدين أقل من 650 كلفن)، ومركب فجوات معقد سالب الشحنة $(V_{Ga}-V_{As})^{-}$ (عندما تكون درجة حرارة التلدين أكثر من 650 كلفن). علاوة على ذلك، فسرت قياسات عمر البوزيترون وجود عنقود كبير من الفجوات المترابطة (vacancy cluster) في المناطق القريبة من سطح العينات.

الكلمات المفتاحية: مطياف فناء البوزيترونات، عيب بلوري، فجوة، توسّع دوبلر، عمر البوزيترون، تلدين.

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Introduction:

Research importance:

Defects cause the material to be n-type, or p-type and affect the recombination rate in the material. With the introduction of crystallographic defects with specific concentrations, one can control the electrical properties of the materials. The story of the defects is the story of the controlling the conductivity and recombination rate in semiconductors and hence making useful electronic devices.

In this study, positron annihilation spectroscopy (PAS) was used to study the defect properties in GaAs thin films. PAS is a very sensitive device for investigating point defects in semiconductors [1]. Positrons are emitted from a radioactive source such as ^{22}Na. If they were injected into the material after its emission, each positron annihilates with electron emitting mostly two 511 keV γ-rays. Open-volume defects such as vacancy-type defects appear like deep trapping centers for positrons. Subsequent changes in specific annihilation parameters of positrons appears when positrons are tripped in vacancy-like defects [2]. Because of reduced electron density in the defects, the lifetime of trapped positrons increases and their momentum distribution becomes narrower [3]. The defect-related lifetime reflects the size of the defect and its concentration. As a result of conservation during the annihilation process, the momentum of the electron-positron pair is transported to the photon pair. The momentum component p in the propagation direction of the γ-rays creates a Doppler shift ΔE of the annihilation energy of 511 ke V. Many annihilation events are measured to give the complete Doppler spectrum, so that the energy line of the annihilation is broadened due to the Doppler shifts in both $\pm$ propagation directions. This effect is used in Doppler-broadening spectroscopy. For more information see [1]. Because of the Doppler-effect, the energy spectrum of the annihilation radiation is broadened. Doppler-effect is conjugated with the momentum of the annihilating e^--e^+ pairs. Positrons, which are tripped, tend to be localized in vacancy-like defects due to the coulomb attraction, which is created from the missing repulsive force of the absent ion cores at the defect site. So, the lattice defects can be exposed by measuring Doppler-broadening spectroscopy of the annihilation radiation, because the electron momentum distribution in such defects changes from that in the defect-free bulk material. The Doppler spectrum is described by two adopted line shape parameters, S and W parameters. These parameters reflect the changes in the low-momentum component and high-momentum component, respectively, at the annihilation site of the electron momentum distribution. The open-volume defects can be realized as an increase or decrease of S(W) parameter comparison with the values of the bulk. The Doppler-broadening spectroscopy (DBS) is found to define the sublattice to which the vacancy-type belongs in compound semiconductors. Furthermore it has information about the chemical surrounding of the annihilation site, and therefore allows the determination of vacancies and vacancy-impurity complexes. Depth-dependent DBS is sensitive to the vacancy-type defects and to the elemental composition of the thin films too. According of this situation, the DBS with a monoenergetic positron beam is an unparalleled experimental technique for determining the defects in thin layers. So far, PAS studies have been done on GaAs thin films and a few on annealed GaAs thin films [4, 5]. The previous studies gave evidence on positron localization at shallow traps in not annealed GaAs. Furthermore, it was observed, that doping GaAs with Si and other elements increases the concentration of a deep positron trap identified as vacancy complex [4, 5].

The Aim and Objectives of the Research:

In this work, PAS and DBS was applied to identify the defects in GaAs semiconductor films annealed under different temperature. It is expected that the increasing of deep defects or of shallow traps is depended not only on doping, but also on the annealing temperature. Thus, doping-related defects in GaAs are key issue to be extensively studied for further development of the material properties. The experimental positron data are matched with theoretical results of the annihilation characteristics based on the atomic superposition calculations to ensure a suitable interpretation. The origin and concentration of the predominant defects could be determined.

Experimental Methods:

In an ultra high vacuum (UHV) chamber were 4 GaAs films co-deposited by molecular beam deposition. The base pressure was between 7×10^{-10} mbar and 7×10^{-11} mbar. As substrate was used $(SiO_2(100\ \text{nm})/Si(100))$, and the thickness of these films was circa 3 μm. The deposition chamber consists of an electron beam evaporator for the evaporation of Ga and an effusion cell for As. An optical detector can controls the flux of Ga immediate. On the other hand the deposition rate of As was controlled by the temperature of the effusion cell. The Ga deposition rate was dominated to achieve the desired nominal composition GaAs. The film thickness was modified by the deposition time. To guarantee homogeneous films, the holder of sample was rotating during the deposition, for more details see e.g. Ref. [6].

Furthermore, the chamber was used for annealing of the GaAs-film samples under UHV conditions. The circular samples (radius 15 cm) were shortly stripped to air and were broken into pieces. Different samples were annealed then for 1 h in UHV up to 700 K , while they were cooled down slowly after each annealing step (annealing temperatures were 500 K, 600 K, 650 K and 700 K), therefore 4 samples were manufactured. To reach the final temperature it was used heating rate by 10 K/min.

The positron annihilation experiments were completed with the slow positron beam system (POSSY) at the Martin-Luther-University in Halle-Wittenberg.

The Doppler broadening spectra of the annihilation radiation as a function of the incident positron energy E was measured. E varied from ~ 0.01 keV to 13 keV, which allows to obtain the defect depth profile. The samples were composed in an ultra-high vacuum (UHV) chamber. High-purity Ge detectors were used for recording the annihilation spectra of conventional and coincidence Doppler broadening spectroscopy. At each positron energy E, a spectrum of $5{\times}10^5$ was collected in the 511 keV annihilation peak. As well known, the Doppler broadening spectrum is characterized by two parameters, S and W. S parameter is calculated as the ratio of the events in the central region of 511 annihilation peak to those under the whole curve and W parameter is the ratio of the events in a fixed energy interval (far from the center) to those under the whole curve. S and W parameters are responsive to the type and concentration of the defect. If positrons are trapped at vacancy defects, S(E) plot increases as a result of this trapping process, for more details see e.g. Ref. [1]. S and W parameters are sensitive to the annihilation with slow and faster electrons, respectively. These parameters allow to distinguish between the different annihilation sites.

Positron lifetime measurements were completed at the positron beam facility NEPOMUC at the Munic Research Ractor FRM II [7]. This system transfers a sharp positron pulse with FWHM= 150 ps with high intensity. The lifetime experiments were executed using the positron beam with an energy of 16 keV, which matches a mean depth of circa 600 µm.

Figure (1) shows scheme of the positron lifetime experiment and the Doppler broadening spectroscopy experiment.

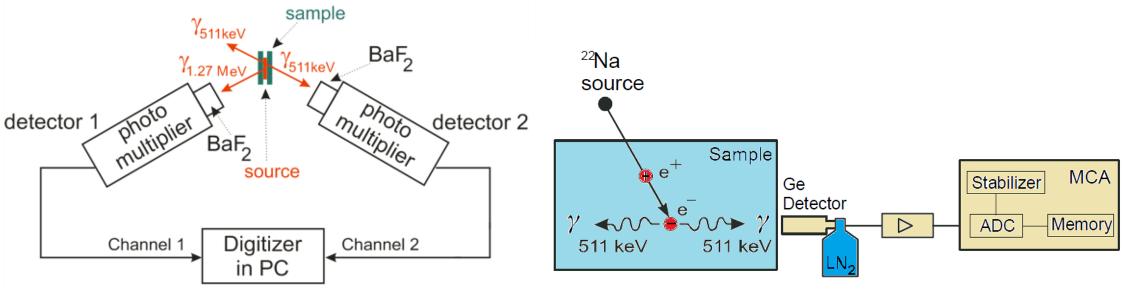

FIG. (1): Scheme of the positron lifetime experiment (left) and the Doppler broadening spectroscopy experiment (right) [1].

Lifetime (LT9) program was used to analyzing the measured spectra [8]. The experimental results were characterized in terms of the average positron lifetime (τ_{av}), which is statistically a perfect parameter since it does not depend generally on the spectra decomposition.

Results and Discussion:

I. Doppler-Broadening results

The defect information in GaAs thin films was gotten by measuring the S parameter as a function of the incident positron beam energy (E). Figure (2) offers the results of Doppler-broadening measurements using slow positron beam of GaAs thin films annealed under different temperatures. The incident positron energy (E) respects the film distance that a positron cross according to the relationship $\bar{z} = A\frac{E^n}{\rho}$ [1]. $\bar{z}$ is the mean implantation depth which is a function of the implantation energy. A and n are empirical parameters. ρ (g cm^{-3}) is the mass density for GaAs.

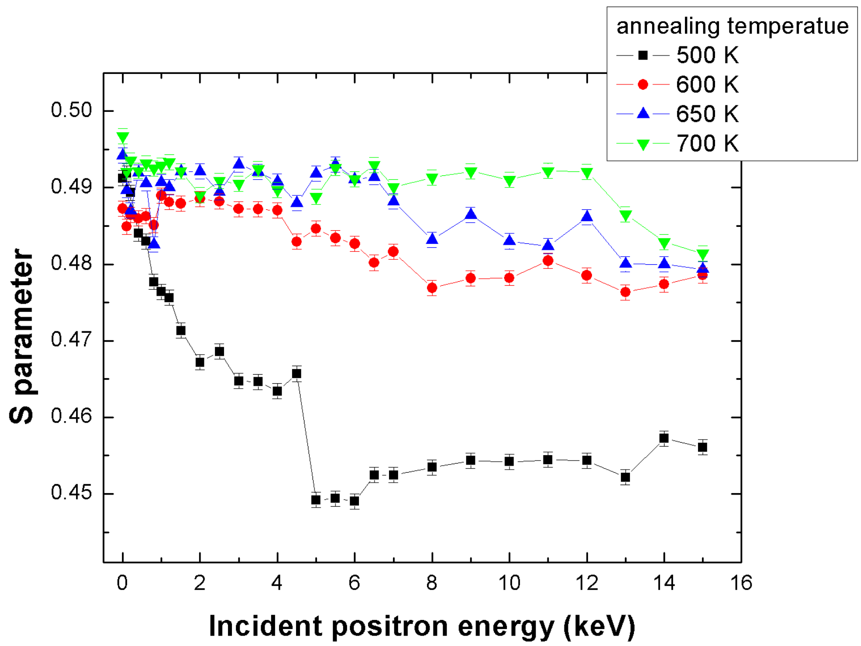

FIG. (2): S parameter as a function of the implanted positron beam energy (E) for various GaAs thin films annealed under different temperatures.

A high value of S parameter is observed at low incident positron energies for all samples, which is corresponding to the positron annihilation at the surfaces of GaAs films. A plateau of S parameter is observed in the energy range (6 to 14 keV), which corresponds to the annihilation of positrons in the bulk region of GaAs films. It is clearly shown that the sample annealed under temperature of 500 K shows values of S parameter lower than that of the other samples. This indicates that this sample contain vacancy-type defects formed during the annealing of the films with extremely lower density relative to the other samples. It should be noted that S parameter in the energy region (~ 0.1 to 2 keV) is relatively higher than its value in the region above 2 keV, indicating the presence of surface defects (shallow traps) in these samples. That also agrees well with the study [4], which revealed that shallow traps exist at the surface of GaAs film. This attributed to the fact that the film stoichiometry at the surface region is different relative to that in the bulk region. At high energies (above 20 keV), the S parameter for all investigated films moves towards a value close to that for the substrate region of each film, therefore it was not investigated. On the basis of the theoretical study [1], the origin of increased S parameter is attributed to the increased amount of defects (not only shallow traps but also vacancies). Furthermore, it is clear that the bulk properties of the GaAs film influence the performance of the GaAs semiconductor. Thus, it is important to investigate the defect properties in the bulk region of GaAs. Average S parameter for each sample was calculated in the incident positron energy range between (6 to 14 keV). This mean S parameter is plotted as a function of the sample annealing temperature as shown in figure (3).

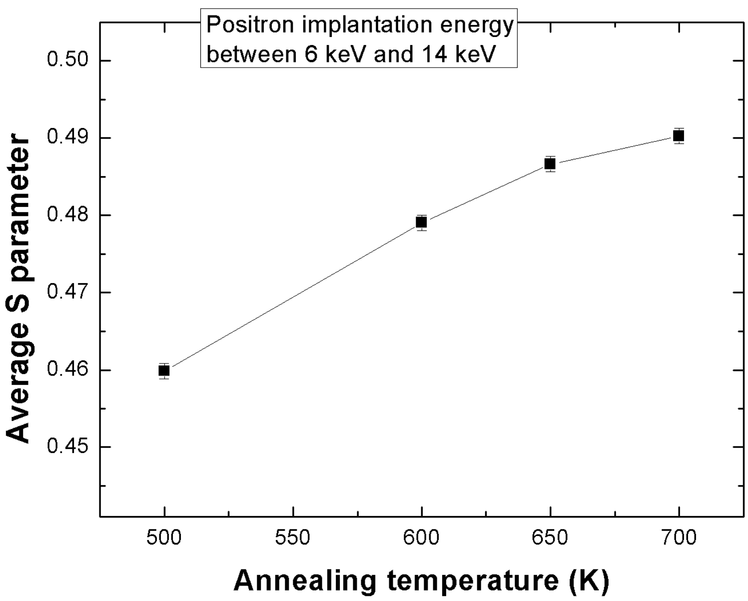

FIG. (3): Mean S parameter at the bulk region as a function of the sample annealing temperature.

The lowest average S parameter belongs to the at 500 K annealed sample. This means, this sample get the lowest density of defects. With increasing the annealing temperature increases the mean S parameter, and thus the deep defect density. Nevertheless, it is difficult to determine the nature of the defect-types observed in the GaAs films by Doppler broadening spectra. Therefore, positron lifetime is performed to identify the properties of the defects observed in the films.

II. Positron lifetime results

The calculation of the electronic structure for the bulk crystal lattice or for a given defect is done within the two-component density functional theory in the generalized gradient approximation (GGA) for the electron exchange and correlation effects. The positron wave function is calculated by fixing the one-particle Schrödinger equation for which the potential is formed using the density of valance and core electron of free atoms in unrelaxed lattice. This potential is formed of the Coulombic and the correlation part. The calculation of momentum distribution is completed through the free atomic wave functions within the model of the independent particles for each state. The final momentum distribution is gotten by selection the summation of the contributions from each electron state weighted by the partial annihilation rates [9]. The positron lifetime is calculated as the inverse of the total annihilation rate calculated from the positron and electron densities. The lifetime is actually calculated for the different vacancies and vacancy complex defects for unrelaxed structure in the GaAs material using atomic superposition method [10, 11], the lifetime calculation results are tabulated in Table (1).

TABLE (1): Theoretically calculated positron lifetime for different defects in GaAs.

Defect	Positron lifetime (ps)
Bulk	231
V_{Ga}	266
V_{As}	267
$2V_{Ga}$	289
$2V_{As}$	292
$3V_{Ga}$	306
$3V_{As}$	308
$V_{Ga} - V_{As}$	332
$(V_{Ga} - V_{As})_2$	341

The positron lifetime measurement for GaAs thin films were done at room temperature by positron lifetime using a beam energy of 16 keV. The lifetime spectra were fitted, and thus three lifetime components were found (Table 2). Figure (4) shows the values of the three lifetimes τ_1, τ_2, τ_3 with their relative intensities. The decomposition of the lifetime spectra is also written in Table (2).

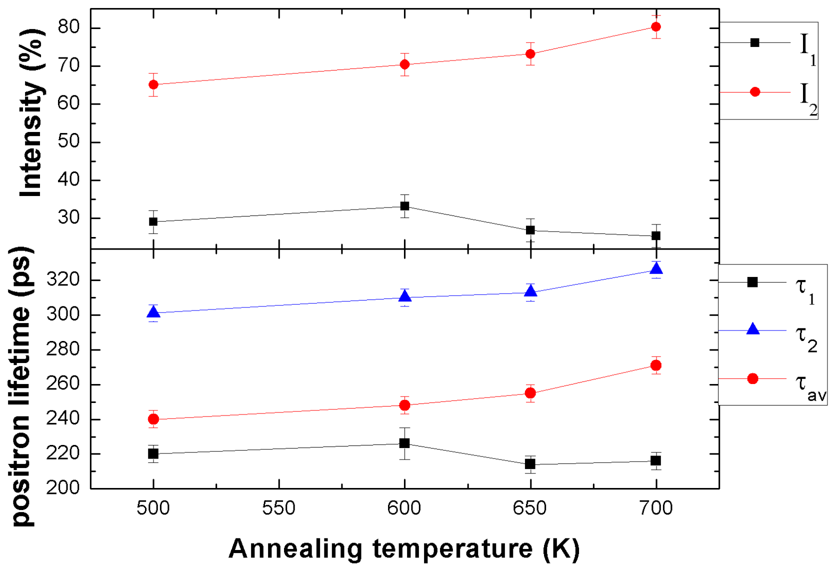

FIG. (4): The decomposition of the lifetime spectra for GaAs samples with different annealing temperature measured at a positron energy of 16 keV.

TA**BLE (2): Decomposed lifetimes of the GaAs samples measured at a positron energy of 16 keV.**

Samples with annealing temperature (K)	Lifetimes and intensities of the components			
	τ_{av} (ps)	τ_1/I_1 (ps/%)	τ_2/I_2 (ps/%)	τ_3/I_3 (ps/%)
500	240	220/29.1	301/65.1	1053/0.81
600	248	226/33.2	310/70.4	1165/0.71
650	255	214/26.9	313/73.2	1020/3.04
700	271	216/25.4	326/80.3	1112/1.07

Because of complicated chemical composition of GaAs thin film and its preparation method, it is difficult to prepare a material without defects in order to define the bulk lifetime experimentally. However, the theoretical calculations determine a bulk lifetime of 231 ps. The first lifetime component (τ_1) achieved for all samples is less than the calculated value of the bulk lifetime (reduced bulk lifetime), and thus it was not taken in consideration [1].

For the second lifetime component τ_2, a lifetime value of 301 ps is obtained in the 500 K annealed sample. In comparison with our calculations, this value cannot be single vacancy such as V_{Ga}, V_{As} or double vacancies such as $2V_{Ga}$, $2V_{As}$, where the lifetime of the single vacancy and double vacancies of the elements composing the GaAs material is in the range of 266-292 ps, as shown in Table (1). The theoretical calculated lifetime for the defect $3V_{Ga}$ is 306 ps. However, the obtained lifetime value agrees well with these calculated values. Therefore, the detected defect in this sample is possible to be $3V_{Ga}$. Its measured intensity I_2 is ~ 65.1 %. The 600 K annealed sample shows a lifetime value of 310 ps. This value is corresponding to the calculated valued of $3V_{As}$. Actually, the measured value is corresponding to the calculated value of $3V_{Ga}$ too. It is very difficult to determine, which vacancy is exactly the correct one. The 650 K annealed sample shows a lifetime of 313 ps, which is higher than but close to the calculated value of the $3V_{As}$. Therefore, we believe that the observed defect in the samples annealed under annealing temperature between 500 K and 650 K is $3V_{Ga}$ or $3V_{As}$. The intensity of the defect of 600 K and 650 K annealed samples is 70 % and 73 %, respectively, which is higher than that obtained in the 500 K annealed sample. This means, that with increasing of the annealing temperature increases the defect density. However, the Doppler broadening measurements support this assumption, as shown in figure (2). The 700 K annealed sample shows a lifetime of 326 ps, which is close to the calculated value of the $V_{Ga} - V_{As}$ vacancy complex. This means, that the annealing affects not only on the defect density but also on the type of defects. Furthermore, the $V_{Ga} - V_{As}$ complex should be negatively charged or neutral to be observed by positron, and therefore the trapping center observed by positron lifetime spectroscopy is a negatively charged vacancy complex $(V_{Ga} - V_{As})^-$. However many studies suggest that vacancy complexes are formed in GaAs thin films to be the deep positron traps [12, 13].

The value of the third lifetime component τ_3 for all samples is larger than the longest lifetime which can be expected for positron annihilation in a solid. This lifetime value means the presence of large cluster of vacancies. The Existence of these lifetimes can be explained by the near-surface defective regions. This is in good agreement with the Doppler-broadening experiments (Fig. (1)), where the samples showed higher values of the S parameter at the surface region. Furthermore, this agrees well with the experimental study by K. Saarinen et al. [4], which revealed that shallow traps exist at the surface of GaAs film.

The average lifetime τ_{av} is found to be 240 ps for 500 K annealed sample and increases with increasing the annealing temperature. This is also an excellent agreement with the Doppler measurements (Fig. (1)), where the samples under higher temperature show higher values of S parameter, i.e. higher defect density.

Conclusions and Recommendations:

The defect properties in GaAs thin films deposited by evaporation process were studied. The influence of annealing temperature on the defect formation is investigated. The defects were tested by PAS using mono-energetic positron beam. Doppler broadening spectra of the annihilation radiation were measured as a function of incident positron energy in the films. Positron lifetime is measured at 16 keV. DBS measurements showed, that with increasing the annealing temperature increases the mean S parameter, and thus the deep defect density. Lifetime measurements confirmed this result. The decomposition of the lifetime spectra of the samples resulted in the detection of two vacancy-related defects: a vacancy $3V_{Ga}$ or $3V_{As}$ (annealing temperature is less than 650 K) and a negatively charged vacancy complex $(V_{Ga} - V_{As})^-$ (annealing temperature is more than 650 K). The value of the third lifetime component τ_3 for all samples interpreted the presence of large cluster of vacancies by the near-surface defective regions.

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