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# Excitonic positronium emission from n-Si(111)

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Recently it was found that energetic positronium (Ps) emission from both n and p type Si(100) occurs primarily via an excitonlike surface state PsX [Phys. Rev. B **84**, 195312 (2011)]. The underlying Ps production mechanism was deduced from the observed Ps emission yield and kinetic energy, using laser and thermally generated electrons to populate the PsX state, but not all of the observed effects have been explained. In this brief report we show that excitonic Ps emission also occurs from n-Si(111), but with characteristics that more closely resemble p-Si(100) than n-Si(100). Considering both (100) and (111) crystal orientations may help in the formulation of a more complete theoretical description of the underlying Ps production mechanism.

Positronium (Ps) is the metastable atomic system composed of an electron and a positron. It has numerous experimental applications [1], and is itself a useful testing ground for bound state quantum electrodynamics (QED) [2]. An efficient method for producing Ps atoms from solid state materials is via thermal desorption from a surface state [3]. In this process positrons implanted into some target material diffuse back to the surface and become trapped in a surface state [4], from which they have some probability of being thermally emitted as a Ps atom [5].

By heating the target material Ps may be formed with almost 100% efficiency in this way [3]. Positronium emitted via thermal desorption will have an Arrhenius type of activation temperature dependence [6], and will have a beam-Maxwellian thermal distribution [7] possibly modified by a velocity-dependent Ps thermal accommodation coefficient or reflection coefficient [8].

It is also possible for Ps to be formed via direct electron capture by positrons leaving the surface [9]. This results in the emission of Ps atoms whose energy does not depend on the sample temperature, and with a yield that does so only via the production of thermally generated traps or defects in the target material [10].

For conductors and semiconductors the direct and thermal processes were thought to be the main Ps production mechanisms, since Ps is generally not stable in the bulk material [11]. It came as something of a surprise, therefore, to discover that Ps emitted from a p-Si(100) crystal had the expected temperature dependent formation probability, but also a constant (i.e., temperature *independent*) kinetic energy [12]. Subsequent experiments with laser induced Ps emission [13] and using different targets [14] support the idea that the presence of a positron on the Si surface creates an attractive potential that can bind a surface electron to form a metastable excitonic surface state (denoted by PsX). Such Ps is emitted with an energy that depends only on the details of the PsX state, and not on the sample temperature. Since electrons need to be excited into this level, the yield may exhibit a thermal

dependence that has form almost identical to the thermal Ps desorption process. Thus, in order to identify the excitonic Ps formation mechanism it is necessary to measure the Ps yield and energy at the same time. Using both laser [15] and lifetime [16] spectroscopy of Ps makes this relatively easy. Moreover, using laser light to populate surface electron [13] states provides further confirmation of the basic physical mechanisms in play.

The idea of a positronic exciton state is closely related to an analogous electronic state that has been observed in Si via two-photon photoemission experiments [17]. In that work, however, it was possible to make very accurate measurements of the electron states populated by short pulsed lasers and measured with an accurate analyzer [18]. Moreover, these mechanisms are well understood theoretically [19]. By comparison, our laser measurements are relatively crude; we use laser pulses that are  $\sim 5$  ns wide and therefore provide almost no information related to the time scale at which different electronic surface states are populated (which is typically a very fast process). Although these electronic activation mechanisms may not be very different from those that occur when there are no positrons present, the positronic state is the only one observed in our experiment (via the production of Ps emission), and so understanding the excitation of electron states when positrons are present on the surface is the key to understanding the Ps formation mechanism.

The experimental procedure is described in detail in ref [14]. Briefly, positrons are captured in a Surko-type buffer gas trap [20] and collected in an accumulator [21]. This allows us to generate intense pulses with  $\sim 2 \times 10^7$  positrons, which are implanted into the target material in  $\sim 1$  ns. The beam has a spot size on target of  $\sim 1$  mm in the 0.16 T magnetic field, and is implanted at an energy of  $\sim 1$  keV. Thus most of the positrons return to the surface where they may form Ps. We use single shot lifetime spectroscopy to determine the amount of Ps produced and measure its lifetime [16, 22]. Then, by measuring changes in the Ps lifetime that are correlated with

the laser wavelength, we measure the Doppler broadened 1S-2P lineshape, and thereby determine the Ps kinetic energy [15].

Our Si samples were prepared the same way as described in ref [14]; that is, they were etched with HF (using a pipette rather than dipping) and rinsed with distilled water. This produces a hydrogen terminated surface which is then installed in the vacuum system. When the hydrogen is present the amount of positronium produced is relatively low, as indicated in Fig 1. In this and subsequent figures the amount of long-lived Ps produced is represented by the parameter  $f_d$ , which approximately proportional to the fraction of incident positrons that form Ps atoms [14].

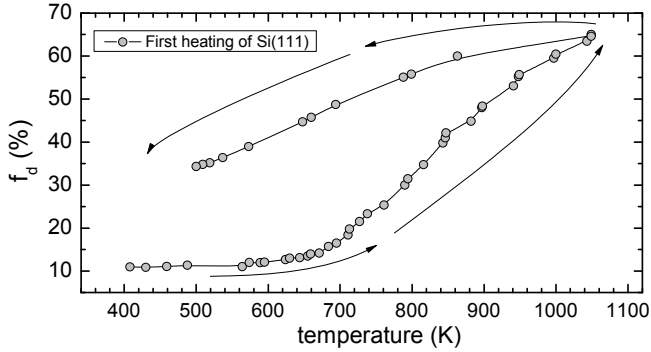


FIG 1. Conditioning of n-Si(111) sample after installing it in the vacuum system. The initial heating serves to desorb hydrogen from the dangling bond states, enabling production of the PsX state, and thus also of vacuum Ps. There are no assigned error estimates to these data.

Surface hydrogen may be desorbed from the Si surface by heating the target to  $\sim 1000$ K. This effect may be seen in Fig 1 which shows  $f_d$  as a function of temperature for n-Si(111) after it was initially installed in the vacuum system [23]. The Ps delayed fraction is initially only  $\sim 10\%$  at room temperature, and increases to  $\sim 30\%$  after one heating cycle. The same effect was seen in all Si samples studied, as well as n-Ge, although in the latter case it was likely Cl that was desorbed [14]. For Si, once the surface hydrogen has been desorbed one may observe the thermally generated Ps emission, as shown in Fig 2. We also show in this figure the previously measured thermally activated Ps for both n and p type Si(100). The thermal activation of n-Si(111) Ps is more like that of p-Si(100) than n-Si(100) with respect to the shape of the temperature dependence. In particular, the n-Si(100) has a local minimum (that was also observed for n-Ge(111) [14]) at  $T \sim 500$  K. The exact mechanism for this has not yet been explained but it is likely to be related to the effect of electric fields on positron diffusion back to the surface [24].

To confirm that the Ps emission from n-Si(111) is indeed taking place via the PsX level we also measured the Doppler width of the 1S-2P transition as shown in Fig 3. This was done with a laser running parallel to the surface (i.e., we measure the Ps kinetic energy associated with the velocity component parallel to the surface). The parameter

$S = [f_d(on) - f_d(off)] / f_d(off)$  is the fractional change in  $f_d$  due to the laser [14], normalised to the delayed signal with the laser off resonance, ( $f_d(off)$ ). The Ps kinetic energy indicated by the Doppler width [12] is shown in meV in the panels of fig 3. Although these data seem to indicate that there is a small change in the Ps energy when heating from 295 to 613 K, this most likely occurs because the total yield is low at room temperature, and the effect of a small ( $\sim 15\%$  [12]) component of fast, directly formed Ps [9] makes the energy appear larger. The same effect was seen in measurements on a p-Si(100) sample, but by decoupling the small direct component it was apparent that Ps produced via the PsX level has a constant energy [12]. At higher temperatures, where the direct component becomes negligible, we see no change in the Ps energy, as was also observed with p-Si(100).

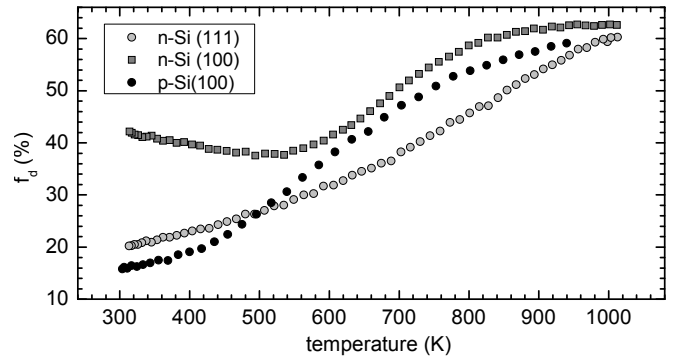


FIG 2. Ps formation as a function of temperature measured for n-Si(111), n-Si(100) and p-Si(100). The error bars are smaller than the symbols used.

In n-Si(100) we found that heating the target actually *cools* the Ps; the Ps energy emitted from this sample is lowered at increasing temperatures until it converges with the thermal value at  $\sim 900$ K. We attributed this effect to shifting of the PsX level due to thermally-induced changes in the electronic surface charge. Clearly the Ps energy cannot be lower than is allowed by a thermal distribution, which means that this effect may be useful if it can be replicated with intense laser induced electronic population of the PsX level on a cryogenic sample surface. This could result in a very efficient source of *cryogenic* Ps, which would be useful for numerous experiments [25]. In particular, laser spectroscopy would be facilitated by reducing the Doppler broadening of Ps atomic transitions [26] and by minimising transit time broadening [2]. Currently it is not possible to produce cold Ps efficiently as the known formation mechanisms either rely on thermal desorption at elevated temperatures [3], utilise surfaces that are delicate and/or unstable at low temperatures [27, 28], or produce hot Ps through non-thermal processes, which then has to be cooled down; this is typically very inefficient with respect to producing Ps below  $\sim 100$  K) [29].

Although we have compelling evidence for the existence of the PsX surface state, some of the aspects of our previous

measurements have yet to be explained. They may depend on subtle details of the mechanisms by which electrons are excited to different surface states, and there may also be effects associated with the condition of the surfaces used in our experiments. Moreover, our explanation of Ps formation via PsX states is almost certainly incomplete. The additional Si(111) data we present here may help to inform a more detailed theoretical description of the mechanism. Also, if we are able produce more than  $10^{12}$  surface positrons per  $\text{cm}^2$  it may be possible to directly observe positron interactions with the electron surface states.

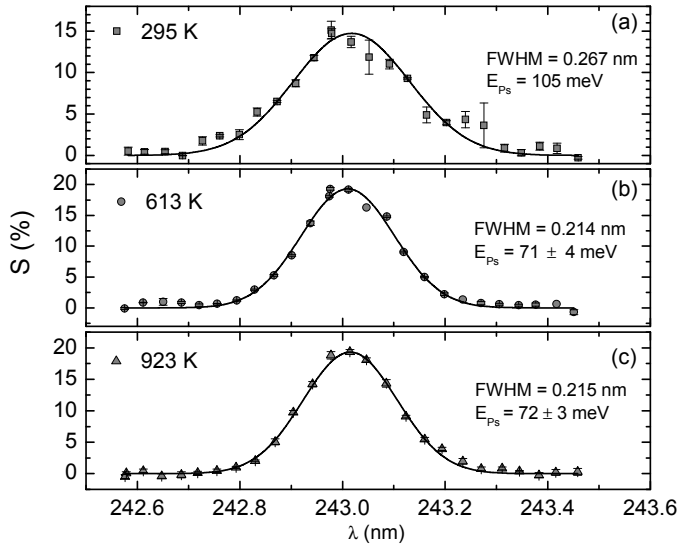


FIG 3. Parallel Ps kinetic energy measured by laser spectroscopy with the beam parallel to the n-Si(111) sample surface at 295 K (a), 613 K (b) and 923 K (c).

There are many unanswered questions that might become clearer in the light of a full theoretical description of the PsX formation mechanism, namely; i) Why does n-Si(111) look more like p-Si(100) than n-Si(100)? ii) What is the reason for the local minimum in the n-Si(100) thermal yield curve? iii) Since the Fermi surface is below the PsX level, why isn't the n-Si(100) yield at its maximum for all temperatures? iv) What role do beam induced electron-hole pairs play in the eventual formation of Ps? v) Are dangling bond states necessary for the PsX level to exist, or can it be supported on other surfaces? vi) Is it possible to manipulate the PsX energy levels so as to produce colder or monoenergetic Ps? vii) What effects will temperature based reconstruction [30] of the crystal have? viii) Will analogous surfaces of Sn(100) and possibly other semiconductors have useful PsX levels? (Note that Ge(100) has been shown to produce Ps via a PsX state [14]).

We have shown that n-Si(111) produces Ps with high efficiency via the PsX positronic exciton level, just as was observed with both n and p type Si(100). We expect that data from two different crystal orientations will be helpful in developing a more detailed theoretical description of this

effect. The possibility of efficiently producing cryogenic Ps (i.e.,  $T \sim 10\text{K}$ ) makes understanding this mechanism an important goal for many experimental programs, including high precision laser spectroscopy and the formation of antihydrogen [25].

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- [1] A. Rich, Rev. Mod. Phys. **53**, 127 (1981).
- [2] S. Chu and A. P. Mills, Jr., Phys. Rev. Lett. **48**, 1333 (1982).
- [3] K. F. Canter, A. P. Mills, Jr., and S. Berko, Phys. Rev. Lett. **33**, 7 (1974); A. P. Mills, Phys. Rev. Lett. **41**, 1828 (1978); A. P. Mills, Jr., Solid State Commun. **31**, 623 (1979).
- [4] K. G. Lynn, Phys. Rev. Lett. **43**, 391 (1979).
- [5] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).
- [6] The exact surface activation energy will depend on the properties of the surface: A. P. Mills, E. D. Shaw, M. Leventhal, R. J. Chichester, and D. M. Zuckerman Phys. Rev. B **44**, 5791 (1991).
- [7] E.g., A. P. Mills, Jr. and L. Pfeiffer, Phys. Rev. B **32**, 53 (1985).
- [8] J. B. Pendry, J. Phys. C: Solid St. Phys. **13**, 1159 (1980).
- [9] A. P. Mills, Jr., L. N. Pfeiffer and P. M. Platzman, Phys. Rev. Lett. **51**, 1085 (1983).
- [10] K. G. Lynn, Phys. Rev. Lett. **44**, 1330 (1980).
- [11] J. Callaway, Phys. Rev. **116**, 1140 (1959).
- [12] D. B. Cassidy, T. H. Hisakado, H. W. K. Tom, and A. P. Mills, Jr., Phys. Rev. Lett. **106**, 133401 (2011).
- [13] D. B. Cassidy, T. H. Hisakado, H. W. K. Tom, and A. P. Mills, Jr., Phys. Rev. Lett. **107**, 033401 (2011).
- [14] D. B. Cassidy, T. H. Hisakado, H. W. K. Tom, and A. P. Mills, Jr., Phys. Rev. B **84**, 195312 (2011).
- [15] D. B. Cassidy, P. Crivelli, T. H. Hisakado, L. Liskay, V. E. Meline, P. Perez, H. W. K. Tom, and A. P. Mills, Jr., Phys. Rev. A **81**, 012715 (2010).
- [16] D. B. Cassidy, S. H. M. Deng, H. K. M. Tanaka, and A. P. Mills, Jr., Appl. Phys. Lett. **88**, 194105 (2006).
- [17] M. Weinelt, M. Kutschera, T. Fauster, and M. Rohlfing, Phys. Rev. Lett. **92**, 126801 (2004).
- [18] M. Kutschera, M. Weinelt, M. Rohlfing, and T. Fauster, Appl. Phys. A **88**, 519 (2007);
- [19] E.g., M. Rohlfing, S. G. Louie, Phys. Rev. B **62**, 4927 (2000).
- [20] C. M. Surko and R. G. Greaves, Phys. Plasmas **11**, 2333 (2004).
- [21] D. B. Cassidy, S. H. M. Deng, R. G. Greaves and A. P. Mills Jr., Rev. Sci. Instrum. **77**, 073106 (2006).
- [22] D. B. Cassidy, in *Physics with Many Positrons*, edited by A. Dupasquier, A. P. Mills Jr., and R. S. Brusa (IOS, Amsterdam/SIF, Bologna, 2010), pp. 1–76.

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- [23] We note that with our sample preparation it is possible that the Si(111) has a  $(7\times 7)$  reconstructed surface, or one of its thermal precursors.
- [24] B. Nielsen, K. G. Lynn, A. Vehanen, and P. J. Schultz, Phys. Rev. B **32**, 2296 (1985).
- [25] J. W. Humberston, M. Charlton, F. J. Jacobsen, and B. I. Deutch, J. Phys. B **20**, L25 (1987); J. P. Merrison, H. Bluhme, J. Chevallier, B. I. Deutch, P. Hvelplund, L. V. Jorgensen, H. Knudsen, M. R. Poulsen, and M. Charlton, Phys. Rev. Lett. **78**, 2728 (1997); P. Perez, *et al.*, AIP Conf. Proc. **1037**, 35 (2008); A. Kellerbauer *et al.* (AEGIS Collaboration), Nucl. Instrum. Methods B **266**, 351 (2008); M. S. Fee, S. Chu, A. P. Mills, Jr., R. J. Chichester, D. M. Zuckerman, E. D. Shaw, and K. Danzmann, Phys. Rev. A **48**, 192 (1993); P. Crivelli, C. L. Cesar, U. Gendotti, Canadian Journal of Physics **89**, 29 (2011).
- [26] D. B. Cassidy, P. Crivelli, T. H. Hisakado, L. Liskay, V. E. Meline, P. Perez, H. W. K. Tom, and A. P. Mills, Jr., Phys. Rev. A **81**, 012715 (2010); D. B. Cassidy, T. H. Hisakado, H. W. K. Tom, and A. P. Mills, Jr, Phys. Rev. Lett. **108**, 043401 (2012).
- [27] A. P. Mills, Jr., *et al.*, Phys. Rev. Lett. **66**, 735 (1991).
- [28] M. S. Fee, *et al.*, Phys. Rev. A **48**, 192 (1993).
- [29] E.g., S. Mariazzi, P. Bettotti, and R. S. Brusa, Phys. Rev. Lett. **104**, 243401 (2010).
- [30] The electronic exciton observed on a Si (100) surface in ref [17] was not observed above 150K, for which the surface reconstruction is different. M. Weinelt, M. Kutschera, R. Schmidt, C. Orth, T. Fauster, and M. Rohlfing, Appl. Phys. A **80**, 995 (2005).