Possible quantum effects in amorphous silicon double Schottky diodes

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Amorphous silicon double Schottky switching diodes in which one contact is vanadium, formed to produce switching, can show discrete steps in the *I-V* characteristics in the ON state. These steps frequently occur at resistances of $h/2ne^2$ where n is an integer. The effect has been found quite strongly at room temperature, whereas in a previous report, only up to 190 K. Other conditions were also significantly different. A small-scale statistical analysis shows that the effect appears to be real. An expression for it is derived based on quantum confinement in small conducting inclusions.

It was recently reported that thin-film amorphous hydrogenated silicon (ASIL) memory structures composed of double Schottky barriers, including a vanadium contact, showed steplike features in the ON state in their current-voltage characteristics.[1] The steps could occur at resistances R corresponding to $h/2ne^2$, where h is Planck's constant, e the electronic charge, and n an integer. The apparent quantized R values were observed at 4 K and, with weakening prominence, at temperatures up to 190 K. This very surprising finding could not be accounted for by the authors with theories of quantized point contacts due to the relatively high temperatures, and no quantitative explanation was offered.

We have repeated these experiments under significantly different conditions to narrow the field for speculation, and also obtained apparent quantum effects. In our cases, the effects were quite prominent even at room temperature. The important question is whether the occurrence of quantized values of R is fortuitous or a real effect. To answer this question requires error estimations and a statistical analysis.

The ASIL was produced by the glow discharge method in a system described previously,[2] in which simple *p-i-n* solar cells of over 5% unoptimized efficiency could be produced. The material showed a 10^5 ratio of photoconductivity (at 1 sun) to dark conductivity, and the hydrogen content, measured by elastic recoil detection, was around 18%.[3] Several kinds of structures were made, namely stainless-steel (SS) -p^+-*n-i*-Al, SS-p^+-*n-i*-Ag, Cr-p^+-Ag, and Cr-p^+-V. Whereas all could be formed to show switching effects, only the latter structure showed step effects, often occurring at quantized resistance values, in agreement with the previous report.[1]

The p^+ layers were 100–350 nm thick, made from silane with 10^4 vppm of diborane. The top and bottom metal electrodes were deposited by vacuum evaporation. The structure is shown in Fig. 1.

In order to make a small area contact, as used in the previous work, we used not lithography but a simpler method in which a thin organic insulator film containing a small hole was placed over the structure and the vanadium evaporated onto this. The nominal device diameter is then that of the 70–100-μm hole in the insulator. This gave a top contact area of $\sim 8\times10^{-5}$ cm^2, two orders of magnitude greater than in the previous work. Although that report stressed that a small area was essential, it is possible that during the forming process only small portions of the nominal area become effective contacts, so that larger evaporated contact areas can be used.

Before obtaining steps in the *I-V* characteristic, it is necessary to "form" the structure and convert it into a switching device. Previously, short pulses were used for forming. In our cases, however, we applied a gradually increasing positive voltage to the vanadium electrode until the resistance dropped suddenly from approximately 10^7 to $\sim 10^3-10^4$ Ω. This usually occurred at 8–15 V. After this forming step, the devices show reversible switching at much lower voltages, typically 2–5. It is also noteworthy that in our cases the devices were switched OFF with a + voltage on the Cr electrode, and ON with a + voltage on the vanadium. This appears to be opposite to the results reported previously.[4] The above-mentioned steps did not occur in every such device but only in some, despite ostensibly identical preparation conditions.

Typical results are shown in Fig. 2. Note that these *I-V* curves were taken at room temperature. Almost all the data to be discussed refer to room temperature. There is usually a small asymmetry in the position of the step, depending upon whether the applied voltage is increasing or decreasing. The integer values of n almost always occurred with the voltage decreasing. Although in many cases n was close to an integer, in some cases it was not. Therefore one must decide the error limits of measurement and determine if values close to an integer are accidental, particularly for the higher values of n where the resistance values are closer together.

In Fig. 2, note the high resistance between zero bias and the first step. This is typical of all the devices, and

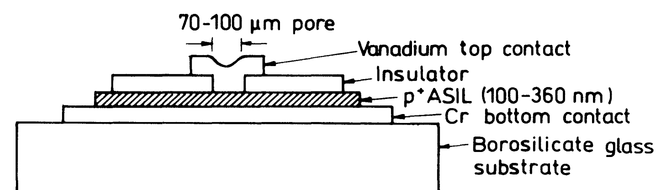

FIG. 1. Schematic diagram illustrating structure of device that shows discrete steps in *I-V* ON characteristic.

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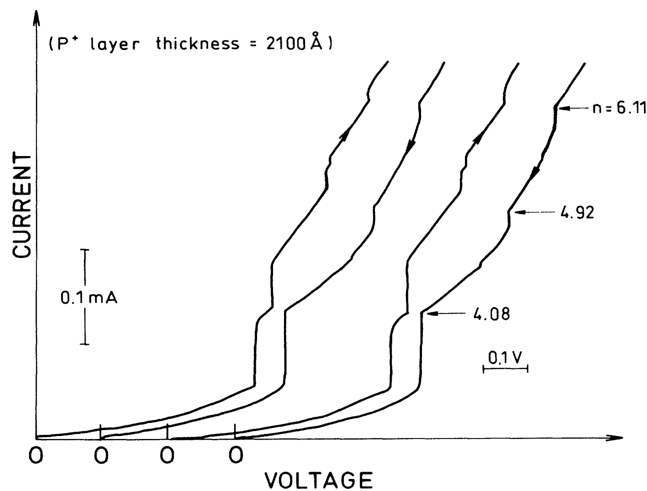

FIG. 2. Current-voltage curves at room temperature for a device, showing hysteresis, and reproducibility over successive up-down cycles of integer steps, where $n = h/(2e^2R)$.

has previously been argued to be due to metal incorporation in the ASIL.[5] In this figure, a current-to-voltage converter was used to measure the current. Distinct reproducible steps can be seen at values of $n = 4.08$, 4.92, and 6.11, with errors of $\pm 3\%$.

Figure 3 shows the resistance versus voltage curves for the device of Fig. 2 and for two other devices at room temperature. One notes that steps occur at values of n covering the range 2–8. Note also that the sizes of the

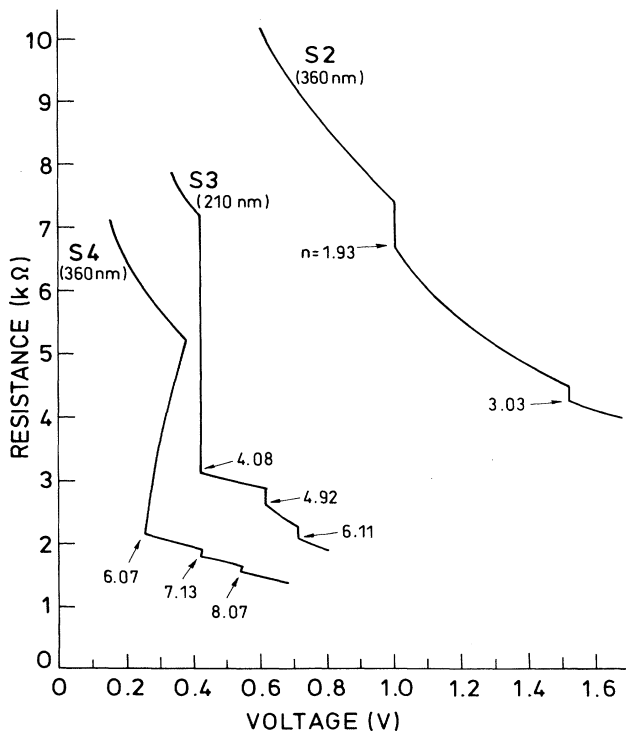

FIG. 3. Resistance R vs voltage for three devices, showing integer steps.

steps and the voltages at which they occur vary among the samples. (A series resistance of 2.62 KΩ was used while measuring sample $S4$, hence causing a small negative slope in that case.)

We turn now to the question of the frequency of integer values of n. In Fig. 4, we show all the values of n that were found for 17 samples, together with their error bars. On the first occasion that a step occurs, n is generally nonintegral in agreement with the previous report.[1] This is believed to be due to the initial sudden change in the conduction mechanism. Hence the values of n which are far from integers and also apply to first steps are circled in Fig. 4 and excluded from analysis. Of the remaining 26 steps, 22 occur at integer values to within measurement errors. There is thus a substantive case for taking the integer values as real.

We assume as before the quantum effects occur in some way that is associated with small filamentary inclusions of vanadium that have entered the ASIL lattice during the forming treatment. The expression $R = h/2ne^2$ can be derived for the case of sufficiently small (quantum-sized) point contacts,[6] and thus this is an attractive hypothesis to attempt to apply to the present results. However, as pointed out previously,[1] such effects have only been observed at temperatures near 1 K, and there are strong theoretical reasons for the effect not occurring at higher temperatures.[7] Our present data, in which steps are clearly observable at 300 K, make that theory even more difficult to sustain. We therefore analyze the phenomena as follows.

Referring to Fig. 5, we consider a number of small inclusions of conductivity higher than that of the bulk ASIL, presumably caused by the forming treatment. Treating each one as small enough to cause significant separation between the electron energy levels, then as the simplest initial assumption we use the energy expression for a particle in a box of width L and of very high potential walls, namely $E_i = h^2 i^2 / (8L^2 m)$, where m is appropriate electron effective mass and i is an integer. This expression is affected by real conditions where the potential is of finite height, allowing conduction to occur between inclusions, but we use the simple form of E_i to show the essentials of the analysis. We assume that there are s equal inclusions between the contacts, and current will flow from the highest filled states E_j in one inclusion to the neighboring one when a voltage is applied such that the lowest empty level in the latter becomes equien-

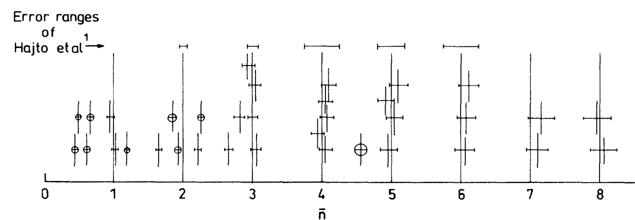

FIG. 4. Values of n for 17 samples, with error bars displayed, staggered to avoid confusion. Measurement error bars quoted by Hajto *et al.* (Ref. 1) are also shown. Circled values apply to first steps which are nonintegral.

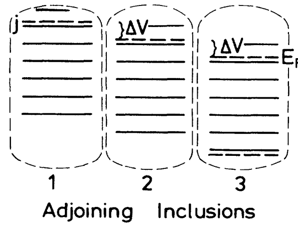

FIG. 5. Schematic diagram of quantized energy levels in adjoining vanadium-rich inclusions, with a voltage increment of ΔV between each pair.

ergetic with the highest filled level in the former, as shown in Fig. 5. Then the current will suddenly increase when the voltage increases by ΔV, where

$$e\Delta V=\Delta E=E_j-E_{j-1}=h^2(2j-1)/(8L^2m)\ . \tag{1}$$

Since the applied voltage $V=s\Delta V$, we have an expression for steps to occur at quantized values of the voltage. For this to hold at a temperature T requires that $\Delta E\geq kT$, i.e.,

$$L\leq[h^2(2j-1)/(8mkT)]^{1/2}\ . \tag{2}$$

The highest filled level E_j approximates the Fermi energy E_F, therefore $h^2j^2/(8mL^2)=E_F$. Combining these conditions yields $j\leq 2E_F/kT$. Since E_F is usually 0.5–3 eV, whereas kT is 0.026 eV at 300 K, this makes j less than 38 or more, and $L\leq 33$ nm, which is reasonable. Hence we have an explanation for discrete steps in the I-V curves that holds at room temperature.

We substitute $x=sh^2/(8L^2me)$. Then the first step occurs at a voltage $V_1=e^{-1}(E_j-E_{j-1})=(2j-1)x$, the second at $V_2=e^{-1}(E_j-E_{j-2})=\{j^2[j-2]^2\}x=\{4j-4\}x$, the third at $V_3=(6j-9)x$, and so forth. If j is reasonably large, say over 10, then, approximately,

$$V_n/2n=(j-1)x \tag{3}$$

for smaller values of n. Therefore one predicts that for a given device, i.e., a given value of j, the quantity $V_n/2n$ is approximately constant. We refer to this below.

In order to derive an expression for the resistance, we need an expression for the current. We take s identical inclusions of dimensions $L\times L\times L$, and make the assumption that the number of conducting electrons per unit volume $N=sn^2L^{-3}$. Clearly N could depend on s, and the assumed dependence on n expresses the quantized increase in the number of conduction electrons that can flow with each extra step in the voltage ladder.

Taking the momentum of a conduction electron as mv, where v is the average velocity, and using $mv=h/\lambda$ where λ is the wavelength, we have, for this electron confined in a dimension L, that $j=2L/\lambda=2mvL/h$. Then the current

$$I=NevL^2=sn^2ev/L\ . \tag{4}$$

Then the resistance

$$R_n=V_n/I=\frac{2h^2jsn}{8L^2me}\frac{L}{sn^2ev}=\frac{h^2}{4e^2Lmv}\frac{j}{n}\ . \tag{5}$$

Since $1/mv=2L/jh$, we obtain

$$R_n=h^2/4e^2L(2L/nh)=h/(2ne^2)\ , \tag{6}$$

as found experimentally, with n being the step index. Without claiming that this theory, with its many simplifications, is ultimate, it is at least a start. Furthermore the above prediction about the constancy of $V/2n$ can be tested.

In Table I we show the experimental values of $V/(2n)$ from six of our room-temperature (RT) samples and four liquid-He temperature samples of Hajto *et al.*[1] For the latter, considering that the voltages were read from small published graphs, the constancy of $V/(2n)$ for a given sample is quite remarkable. In our RT cases, four samples show agreement and two do not. The worst fit for both the 4- and 300-K cases is generally at the first value of n, which may be related to initiating phenomena.

If one takes the view that the data at 4 K provide a more stringent test, since at 300 K there could be more thermally activated transitions between inclusions, then the data of Table I seem to be consistent with the theory.

The number s of the inclusions can be derived from Eq. (4), since $s=LI/(nev)$. Taking L of 33 nm for $E_F=0.5$ eV, then for our sample 3, where $I=0.061$ mA at $n=3$, one obtains $s=9.97$, i.e., 10, which seems reasonable.

TABLE I. Experimental values of $V/(2n)$ for various samples.

Authors	Sample	$V/(2n)$ $n=2$	3	4	5	6	7	8
Hajto *et al.*[a]	Fig. 6, curve *a*			0.058	0.065	0.065		
(all at 4 K)	*b*	0.093	0.072	0.063	0.069	0.065		
	c	0.110	0.078	0.070	0.072	0.067		
	d				0.053	0.054	0.055	
This work	1					0.022	0.030	0.033
(all at 300 K)	2		0.043	0.063	0.085			
	3		0.043	0.055	0.054			
	4						0.027	0.027
	5			0.043	0.086	0.12		
	6			0.051	0.063	0.059		

[a]Reference 1.

Similar values apply at other points.

We comment briefly on the physical basis for the assumption of inclusions of vanadium-rich material of equal sizes. These sizes are determined by factors such as solubility, interfacial segregation coefficients, and free energy of the boundaries, which are currently unknown. Direct experimental determination is difficult due to the small sizes. However, the phenomenon of small islands or voids of similar sizes is not unusual. See, for example, the transmission electron micrographs of amorphous hydrogenated Si and Ge alloys shown by Paul,[8] and the display of voids in ASIL by Danesh and Pantchev.[9] Many of these are of closely similar size.

In conclusion, our data, taken from samples prepared differently, support the previous report[1] of quantum effects but extend it to 300 K. We provide an analysis of the data that appears consistent and predicts a relation between numbers and sizes of conducting inclusions.

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[1]J. Hajto, A. W. Owen, S. M. Gage, A. J. Snell, P. G. LeComber, and M. J. Rose, Phys. Rev. Lett. **66**, 1918 (1991).

[2]D. Haneman and D. H. Zhang, Phys. Rev. **35**, 2536 (1987).

[3]A. Hoffman, D. D. Cohen, M. Jafar, and D. Haneman (unpublished).

[4]M. J. Rose, J. Hajto, P. G. LeComber, S. M. Gage, W. K. Choi, A. J. Snell, and A. E. Owen, J. Non-Cryst. Solids **115**, 168 (1989).

[5]S. M. Gage, J. Hajto, S. Reynolds, W. K. Choi, M. J. Rose, P. G. LeComber, A. J. Snell, and A. E. Owen, J. Non-Cryst. Solids **77/78**, 1373 (1985).

[6]B. J. van Wees, H. van Houten, C. W. J. Beenakker, J. G. Williamson, L. P. Kouwenhoven, D. van der Marel, and C. T. Foxon, Phys. Rev. Lett. **60**, 848 (1988).

[7]T. Ando, Phys. Rev. B **44**, 8017 (1991).

[8]W. Paul, in *Amorphous Silicon and Related Materials,* edited by H. Fritzsche (World Scientific, Princeton, NJ, 1989), p. 63.

[9]P. Danesh and B. Pantchev, in *Amorphous Silicon and Related Materials,* edited by H. Fritzsche (World Scientific, Princeton, NJ, 1989), p. 81.