(1965).
[9]A. Zangwill and Paul Soven, Phys. Rev. A 21, 1561 (1980).
[10]P. Rabe, K. Radler, and H. W. Wolff, in *Vacuum UV Radiation Physics*, edited by E. E. Koch *et al.* (Vieweg-Pergamon, Berlin, 1974), p. 247.
[11]H. W. Wolff, R. Bruhn, K. Radler, and B. Sonntag, Phys. Lett. 59A, 67 (1976).
[12]We employ the exchange-correlation potential suggested by O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
[13]To our knowledge, no absolute measurements of rare-earth cross sections exist. Such measurements would be desirable for direct comparison with our calculations.
[14]M. Hecht and I. Lindau, to be published.
[15]This is true for the region of space most important for the matrix elements, i.e., near the polar axis.

Memory Effect in Field Emission from the W-EuS System

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(112) planes of W–amorphous-EuS field emitters exhibit a memory effect in the current-voltage characteristics, the actually drawn current being "locked in." In contrast to Ovshinsky-type memory switches, self-stabilization of the electron current occurs due to negative space charge. Measurements of the electron-spin polarization exclude a thermally induced mechanism. To our knowledge these memory structures are the smallest in solid-state physics.

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Amorphous (glassy) semiconductors are beginning to be understood to such a level that devices with desired properties can now be fabricated. The initial scepticism of both scientists and engineers towards the discovery by Ovshinsky[1] and others[2] has been slowly replaced by an optimistic approach especially because of the considerable recent progress in the physics of glassy materials. We mention here the Ovonics, which are memory devices made of an amorphous thin film of, for example, $Te_{40}As_{35}Ge_6Si_{18}$ sandwiched between two metal electrodes. By applying a voltage greater than the threshold value, these devices switch into a low-impedance state with only a small voltage drop across the structure.

We report in this paper the observation of a memory effect in a system consisting of a tungsten field emitter with an evaporated, highly disordered EuS layer on top of it. The investigation was performed in order to understand the different switching processes that occur within the W/EuS field-emission system,[3] which is also a powerful source for polarized electrons.

We attribute the memory effect to an electronic process. Switching effects involving rare-earth compounds have also been reported for highly doped EuO (Ref. 4) and EuS (Ref. 5). The basic differences of the present structure when compared with those reported so far are the following: (1) The dimensions are very small (1000 times smaller than the Ovonics). It is not even the small field emitter but only its (112) planes which display the effect. (2) Only one electrode is in contact with the insulating amorphous material. (3) The substrate is a single crystal and is atomically clean before the evaporation of the EuS film. (4) The electrons tunnel into the vacuum, and can therefore be analyzed with respect to their spin or energy, thus offering novel possibilities for the investigation of tunneling phenomena.

The experimental setup consists of an apparatus which is basically a modified field-emission microscope with a probe hole in the fluorescent screen for measuring either the electron-spin polarization or the electron current of a selected part of the field-emission pattern. The electron current is detected by an electron multiplier to increase the sensitivity. For spin-polarization analysis the apparatus was connected to a "Mott" detector. The tungsten tip is mounted on a liquid-helium–cooled cold finger with an improved cooling system as compared to the original design,[6] allowing selection of a stable tip temperature in the range 4–50 K. The temperatures above 4 K are obtained by resistive heating with a carbon resistor which is glued to the heat exchanger rather than by reducing the helium flow rate.

EuS can be evaporated onto the clean field emitter by means of an electron-beam–heated oven, which can be moved in front of the tip. After evaporation of the EuS, the emitter is annealed as follows: The freshly coated emitter is cooled to 4 K. After the liquid-helium supply is turned off, a high current (8 A) is passed through the filament supporting the tip until the desired annealing temperature is reached.[7] The temperature is kept for a few seconds on this level before the heating current is switched off. During this process only the thin front bow of the filament becomes hot. Therefore, the emitter cools down very rapidly with an estimated initial rate of 3000 K/sec after the current is turned off (see Ref. 7, Fig. 3).

The initially evaporated EuS layer is about 500 A thick. The actual film thickness may be lower since the film could become thinner during the annealing process.

The emitter characteristics depend strongly on the annealing temperature[8]: The dependence of the emission current on extraction voltage $I(V)$ for emitters annealed below 1000 K is well defined and, especially for annealing at 800 K, is described by a Fowler-Northeim equation as for clean metal field emitters. Annealed between 1000 and about 1200 K, the $I(V)$ curve displays the reproducible "memory effect" as is shown in Fig. 1. At constant tip temperature the emission current is very small below a threshold voltage V_{on} and increases rapidly with increasing voltage.

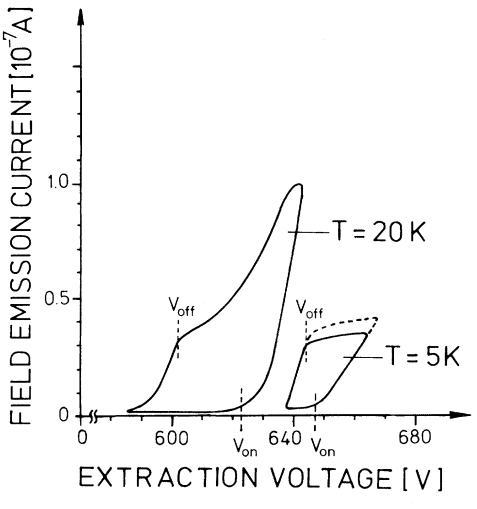

FIG. 1. Current-voltage characteristics of a W-EuS field emitter annealed at 1000 °C, measured at 5- and 20-K tip temperature.

On reducing the voltage the reached current level is maintained until a minimum holding voltage V_{off} is applied. Below V_{off} the current decreases sharply. V_{on} is only 20–25% of the voltage which is necessary to obtain the same current from the clean tungsten emitter.

The field-emission pattern generally displays just one small, bright spot on the otherwise dark screen. At higher extraction voltage other spots appear which together with the first one are arranged with the symmetry of the (112) planes of the underlying tungsten emitter.[9]

In Fig. 1 $I(V)$ characteristics are shown for tip temperatures of 5 and 20 K. The shapes of the loops are rather different for the different temperatures and the threshold voltage V_{on} is much smaller at the higher temperature. The electron-spin polarization P of the field-emission current selected by the probe hole was $P = 60\%$ at 5 K.

The observed high electron-spin polarization excludes the thermal model for the on state, according to which the free carriers are produced by local heating of the structure to 800–900 K,[10] since the Curie point even of nonstoichiometric EuS is known to be well below 150 K.[11]

The strong dependence of the threshold voltage on emitter temperature, especially below 20 K, shows that the memory effect must be electronic in nature. The occurrence of a current-voltage hysteresis cannot be explained with free-electron tunneling models; there must be localized electric charges present. We interpret the observations on the basis of the one-dimensional emitter model shown in Fig. 2. The EuS Fermi level is pinned to the tungsten Fermi level by electron transport from the EuS to the tungsten tip.

We consider the EuS layer to be strongly dis-

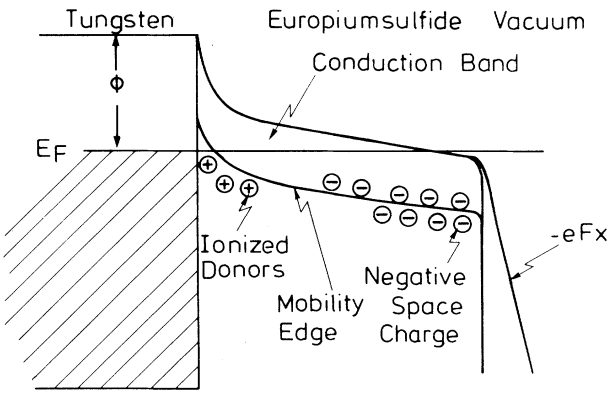

FIG. 2. One-dimensional band model for the W–amorphous-EuS field emitter (schematic).

ordered or "amorphous" because of frozen-in dislocations, occurring with the high annealing temperature. The transition of samples annealed near 800 K from the crystalline to the amorphous phase can be observed by measuring the dependence of emission current on tip temperature at constant extraction voltage. Samples which are annealed near 800 K, display an increase in current on cooling below 17 K by about three orders of magnitude. Since the Curie point of crystalline, pure EuS is at 16.5 K,[11] we conclude that these EuS layers are well ordered. The characteristic current increase on cooling vanishes gradually when the emitter is annealed at a higher temperature,[12] and the Curie point increases. The samples studied here have lost the current-increase property which we attribute to strong disorder.

Amorphous semiconductors are described by means of conduction bands and valence bands, but the band gap (which is called the "mobility gap" for amorphous substances) is filled with *localized* states, which can act as donors and acceptors.[13] The donor states are the sulfur vacancies, which are known to be able to bind two electrons.[14]

An external positive electric field, which penetrates into the insulating EuS, will then ionize the donors due to Zener tunneling. For a small applied electric field, the ionized traps will be refilled in a time shorter than the ionization time. In this region we are still in the off state. At a critical field of about 10^5 V/cm (Ref. 15), the ionization rate will become greater than the recombination rate and a positive space charge builds up, which increases the injected electron current.

Under these conditions, the ovonics would go into the on state, which produces a dramatic drop of voltage across the junction. Without including a series resistor into the circuit, the ovonics would be destroyed. In contrast the current for the tungsten EuS system need not be externally limited. For the extraction voltages shown in Fig. 1 the current is stable at any value. We conclude that the current limits itself by negative space-charge buildup inside the EuS layer.

The negative space charge does not compensate the positive one at the W-EuS interface. The injected electrons are, in fact, "hot" and have a high velocity, thereby yielding only a small space charge. Inelastic scattering slows down the injected electrons on their way through the EuS layer and they are trapped so that the negative space charge will primarily accumulate near the vacuum interface.

The model described above is also supported by the shift of the $I(V)$ characteristic to lower voltage with increasing temperature (Fig. 1). According to the magnetic impurity model of Kasuya and Yanase[16] one of the two electrons trapped in a sulfur vacancy orders the surrounding $4f^7$ spins of the Eu^{++} ions ferromagnetically, forming a giant spin molecule. The binding energy of the trapped electron is $E = -\vec{\mu}_B \cdot \vec{J}\langle S_z\rangle$, where $\langle S_z\rangle$ is the mean value of the surrounding $4f^7$ spins and J the ferromagnetic coupling constant. The lower the temperature, the tighter will the impurity electron be trapped due to magnetic ordering, and a higher extraction voltage is required to obtain the same current. A purely thermal explanation for the current increase is excluded since the $I(V)$ characteristics do not shift to lower energy with higher tip temperature.

The $I(V)$ curve for the tip at 20 K increases steeper than the 5-K curve. We consider this to be caused by a diminishing of the number of traps at the higher temperature because of the vanishing of the magnetic binding energy. The highest trap levels thus become degenerate with the conduction bands, and we reach the case of "space charge with low trap density" as defined by Geppert,[17] which results in a much steeper $I(V)$ characteristic.

Our model is also consistent with the double-injection model for the ovonics as proposed by Mott[18] and Henisch.[19] In that model electrons are injected from one electrode and holes from the other one, so that any space charge will be compensated in the interior of the layer. This results in the small on voltage across these devices. In the W-EuS system only electrons are injected, and the missing hole injection is considered to be responsible for the large negative space charge which stabilizes the electron current.

The important observation of the "current lock-in," as is evident from Fig. 1, is explained as follows: The charge distribution inside the EuS layer and at the W/EuS interface adjusts itself to deliver the current. In this equilibrium condition, the ionization and recombination rates are equal. Increasing the external field increases the electric field at the interface and hence also the number of ionized traps becomes larger, resulting in the higher tunnel current. Reducing the external voltage does not diminish the positive space charge since the recombination rate near

the interface is very small because of the high electron velocity.[2] Thus, the charge distribution "locks in," and also the electron current, which depends on the charge distribution rather than on the extraction voltage.

According to the above arguments, the memory effect would not necessarily be specific for the (112) planes, although we did not observe it to occur for other directions. We interpret this apparent specificity as being caused by a local reduction of the height of the potential barrier near the (112) planes at the W/EuS interface. With increasing extraction voltage, the effect is first observed for the planes with the smallest barrier. The reason for the local work-function lowering is probably the same as for CsO or ZrO on W.[20,21] In those systems, the W(112) planes are unique in the sense that the negative ions fit into the W-lattice voids and that the number of adsorbed positive ions equals the number of W-O bonds, resulting in the smallest binding distance between the positive and negative ions. This yields a larger work-function reduction for the (112) planes than for other planes. The especially strong reduction of the W(112) work function with EuS on W is observed most clearly for emitters annealed above 1200 °C, when all (112) planes appear as bright spots on the otherwise dark fluorescent screen.[22] In this very high annealing temperature case a memory effect is not observed, indicating that the EuS layer has become very thin.

We conclude our discussion by comparing some of the characteristics of the ovonics and of the W/EuS system. The fact that the W/EuS structures store the value of the actual current drawn shows that in principle more than one bit of information can be stored in memory cells, if hole injection can be suppressed.

Since the emission is strongly confined to W(112) faces under the present experimental conditions, we estimate the cross section of the conducting filaments to be about 100×100 Å^2. This suggests for the first time that with amorphous materials much smaller memory structures may be possible than with doped crystalline semiconductors. In fact, for the latter the dimensions cannot be made much smaller than the volume which contains at least several impurity atoms, which results in minimum dimensions of at least 1000×1000 Å^2.

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[1]S. R. Ovshinsky, Phys. Rev. Lett. 21, 1450 (1968).
[2]For a recent review, see D. Adler, H. K. Henisch, and N. F. Mott, Rev. Mod. Phys. 50, 209 (1978).
[3]E. Kisker, G. Baum, A. H. Mahan, W. Raith, and B. Reihl, Phys. Rev. B 18, 2256 (1978).
[4]P. Wachter, Phys. Lett. 41A, 391 (1972).
[5]E. Bayer, Phys. Status Solidi (b) 80, 57 (1975).
[6]D. A. Reed and W. R. Graham, Rev. Sci. Instrum. 43, 1365 (1972).
[7]E. Kisker, J. Phys. E 11, 697 (1978).
[8]E. Kisker, G. Baum. A. H. Mahan, W. Raith, and K. Schroeder, Phys. Rev. Lett. 36, 982 (1976).
[9]We have observed the memory effect only for ⟨112⟩ directions of the underlying tungsten emitter. We did not study quantitatively the intensity variation of the surrounding dark background [which remains dark when a (112) plane is switched on]. It can not be excluded that for other experimental conditions the effect may occur also for other planes.
[10]D. M. Kroll and M. H. Cohen, J. Non-Cryst. Solids 8-10, 544 (1972).
[11]E. Bayer and W. Zinn, Z. Angew. Phys. 32, 83 (1971).
[12]E. Kuhlmann and E. Kisker, J. Magn. Magn. Mater. 13, 209 (1979).
[13]N. F. Mott, Philos. Mag. 19, 835 (1969).
[14]This is generally accepted for the similar case of EuO; see, e.g., T. Penney, M. W. Shafer, and I. B. Torrance, Phys. Rev. B 5, 3669 (1972).
[15]N. F. Mott, Philos. Mag. 32, 159 (1975).
[16]T. Kasuya and A. Yanase, Rev. Mod. Phys. 40, 684 (1968).
[17]D. V. Geppert, J. Appl. Phys. 33, 2993 (1962).
[18]N. F. Mott, Contemp. Phys. 10, 125 (1969).
[19]H. K. Henisch, Sci. Am. 221, 30 (1969).
[20]L. W. Swanson and R. Strayer, J. Chem. Phys. 48, 2421 (1968).
[21]L. R. Danielson and L. W. Swanson, Surf. Sci. 88, 14 (1979).
[22]W. Eckstein, K. F. Georg, W. Heiland, J. Kirschner, and N. Müller, Z. Naturforsch. 25a, 1981 (1970).