JOURNAL OF MATERIALS SCIENCE 24 (1989) 2493–2496

Elaboration and characterization of amorphous V_2O_5 thin films–silicon p–n junctions

C. GLEDEL, J.-P. AUDIERE*, R. CLEMENT
Laboratoire de Spectrochimie des Eléments de Transition (CNRS UA 420), Université de Paris-Sud, 91405 Orsay, France

Unusual p–n junctions have been obtained by vapour deposition of amorphous V_2O_5 thin films on monocrystalline p-type silicon wafers and their current–voltage characteristics have been studied. The efficiency of such diodes and the effect of illumination are shown to depend strongly on the parameters of the evaporation process. Results are discussed, with particular emphasis on the role of the electrical charge mobilities.

1. Introduction

Amorphous vanadium pentoxide has been extensively studied since the discovery of its semiconducting properties. A number of methods have been explored to obtain this material such as splat cooling [1, 2], sputtering or vapour deposition [3, 4]. In all cases, V^{4+} ions are produced as a consequence of the creation of oxygen vacancies and electrical transport arises through a polaronic mechanism, in agreement with the ionic character of the lattice [5].

In the course of a general study of the electrical properties of amorphous V_2O_5 thin films prepared by vapour deposition [5–7], we have examined the possibility of preparing p–n junctions by vapour deposition of amorphous V_2O_5 (n-type semiconductor) films on the surface of monocrystalline p-type silicon wafers. In addition to possible technological interest, such devices offer a mean to study the validity of applying the usual band model picture to the description of such particular p–n junctions involving localized states of the d electrons of the V^{4+} ions.

2. Experimental procedure

2.1. Strategy for material optimization

It has been shown in previous papers [5] that amorphous vanadium pentoxide thin films prepared by evaporation under vacuum (vapour temperature, $T_V = 840°\,C$) exhibited two distinct series of compounds.

The first one was obtained by efficient quenching of the vapour onto a substrate held at various temperatures (T_S), from $-196°\,C$ to $+120°\,C$. The films prepared under these conditions were amorphous and exhibited a glass transition T_g ($\simeq 300°\,C$), and a multistep crystallization at about 340° C.

The second series, obtained with a weaker quenching of the vapour ($T_S = 180$, 240 or 300° C) consisted of pseudo amorphous thin films already containing small nuclei. Such films are considerably less stable and they have been discarded in the present work.

Among the various materials available in the first series, only films deposited onto a substrate held at 20 and 120° C have been used in the present work, the main reason being that the mechanism of electrical conductivity has been properly established in these cases [5]. The films deposited on substrates held at low temperature have been discarded because they exhibit numerous amorphous–amorphous relaxations [5] (which prevent the fitting of conductivity data) and also because their conductivity is smaller.

The vapour temperature in the Joule evaporation has been fixed at 840° C, as in [5]. This value represents a compromise between a too slow evaporation rate and a too high V^{4+}/V_{total} ratio R which would lead to the formation of other oxides such as V_3O_7, V_4O_9 and V_6O_{13} as a result of large oxygen losses according to the equilibrium

$$V_2O_5 \rightleftharpoons V^{4+}_{2\varepsilon}V^{5+}_{2(1-\varepsilon)}O_{5-\varepsilon} + \frac{\varepsilon}{2}O_2$$

(R is about 1.4% under such conditions [5]).

As the conductivity of the films depends on the concentration of adjacent V^{4+}–V^{5+} site pairs, it is nevertheless interesting to modify the R ratio and the only accessible way to increase it is to realize films of ternary compounds such as $Li_xV_2O_5$ instead of pure V_2O_5. This in turn requires that flash evaporation be used [6] (instead of progressive Joule heating), in order to keep in the deposited film the stoichiometry of the starting material. The composition $Li_{0.1}V_2O_5$ was chosen because it corresponds to a maximum of the conductivity.

2.2. Experimental features

According to the above discussion five different films were deposited under conditions which are summarized in Table I.

The evaporation plant and the flash evaporation device have been already described [3–7]. The amorphous thin films have been deposited onto freshly

---

*To whom all correspondence should be addressed.

0022-2461/89 $03.00 + .12 © *1989 Chapman and Hall Ltd.*

TABLE I Conditions of vapour deposition

Thin film	Composition of starting material	Evaporation mode	T_V (°C)	T_S (°C)	$\mu^{[5,7,8]}$ ($cm^2 V^{-1} sec^{-1}$)	$\sigma^{[5,7,8]}$ ($\Omega^{-1} cm^{-1}$)
1	V_2O_5	Joule	840	20	1.53×10^{-7}	6.12×10^{-6}
2	V_2O_5	Joule	840	120	8.45×10^{-7}	3.38×10^{-5}
3	V_2O_5	Flash	1050*	20	1.16×10^{-6}	4.50×10^{-5}
4	V_2O_5	Flash	1050*	120	1.25×10^{-5}	5.00×10^{-4}
5	$Li_{0.1}V_2O_5$	Flash	1100*	20	2.48×10^{-6}	1.40×10^{-4}

*It is necessary to maintain the crucible temperature (i.e. the vapour temperature T_V) at higher temperature (1050–1100° C instead of 840° C) in order to ensure the best flash conditions. Nevertheless, the R ratio for pure V_2O_5 does not exceed 1.5%.

cleaned p-type silicon substrates (10^{17} carriers cm^{-3}), and their thicknesses were measured using an optical microscope equipped with a Mirot interferential device. Typically, the films were 300 nm thick. The silicon wafers were supplied by Thomson C.S.F. Company, L.C.R. Corbeville, Orsay, France. Electrical contacts were ensured by an Au–Ga deposit onto the silicon and a gold, combshaped deposit on the amorphous thin film (Fig. 1). This shape of electrode allowed electrical measurements to be performed under illumination of the interface between the amorphous oxide film and the silicon substrate. D.c. current–voltage characteristics were obtained using a Tektronix 577. Photocurrents were measured under an illumination power of about 40 mW cm^{-2} from an incandescent lamp.

3. Results

3.1. Junctions based on "Joule evaporated" V_2O_5 (Films 1 and 2)

The voltage–current characteristics of the junctions obtained from Films 1 and 2 are shown in Fig. 2. The *V–I* characteristic obtained with the more-quenched Film 1 (T_S = 20° C) is typical of a diode (rapid increase of current with voltage under direct bias, almost null current under reverse bias). Light increases the current in direct bias, but has no significant effect under reverse voltage.

The less-quenched Film 2 (T_S = 120° C) displays significantly different results. In darkness with direct bias, current increases rapidly in the range 0–1 V and then linearly at higher voltage. Under reverse bias the junction gives a small but non zero current (– 0.4 mA for – 3 V). In contrast to the results obtained with Film 1, light exerts a drastic effect, particularly under reverse bias, as shown in Fig. 1.

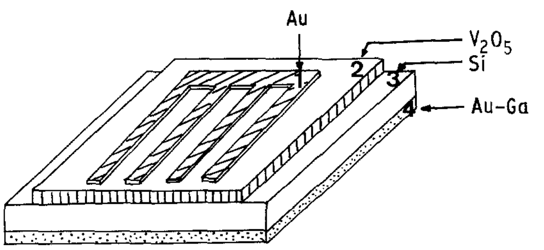

Figure 1 The vanadium pentoxide–silicon junction: experimental device. (1) Gold combshape top electrode; (2) V_2O_5; (3) Si; (4) Au–Ga electrode.

3.2. Junctions based on "flash evaporated" V_2O_5 (Films 3 and 4)

The characteristics of these junctions (Fig. 3) are quite similar to the previous ones, but some differences can be noted:

1. Film 3 in darkness and direct bias gives identical results to Film 1, and very close results under reverse bias.
2. Illumination of Film 3 has no effect in direct bias and causes a moderate current increase in reverse bias, which is the opposite of the features observed with Film 1.
3. The less quenched Film 4 has a behaviour which recalls that of Film 2, but with a diode effect still weaker. The influence of light is also very weak.

It is interesting to note that the diodes obtained using Films 1 and 3 tolerate a reverse voltage down to – 50 V without any damage.

3.3. Junctions based on $Li_xV_2O_5$ (Film 5)

The characteristic of the junction obtained with Film 5 (Fig. 4) shows a very poor rectifying effect and, above all, a much smaller current. Light increases the current under reverse bias, but has no effect under direct bias.

4. Discussion

It has been shown that local order in pure V_2O_5 amorphous thin films is nearly the same as in the crystalline orthorhombic material [8]. The junction between vanadium pentoxide and the silicon substrate is

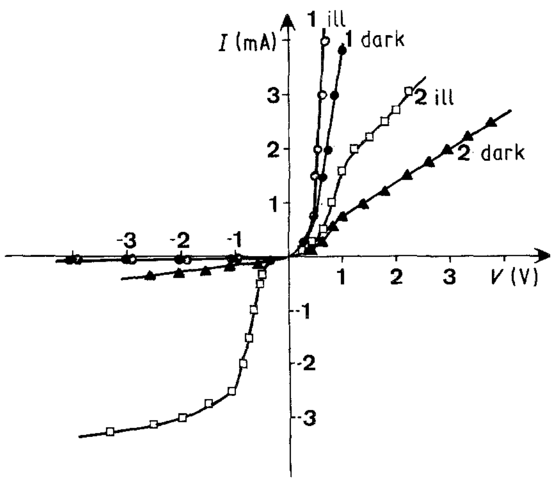

Figure 2 D.c. voltage–current characteristics of the junctions using V_2O_5 Films 1 and 2: (●) Film 1, no illumination; (○) Film 1 illuminated; (▲) Film 2, no illumination; (□) Film 2 illuminated.

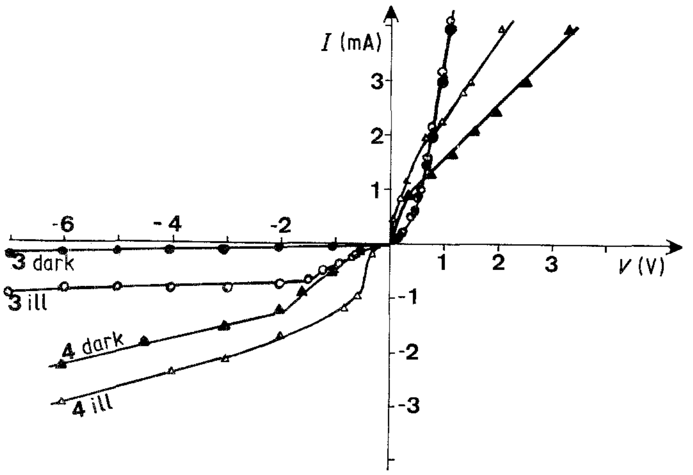

Figure 3 D.c. voltage–current characteristics of the junctions using V_2O_5 Films 3 and 4: (●) Film 3, no illumination; (○) Film 3 illuminated; (▲) Film 4, no illumination; (△) Film 4 illuminated.

consequently made up with an orthorhombic deposit in contact with a cubic substrate. This conformation necessarily induces crystallographic defaults at the deposit–substrate interface. Moreover, the preparation mode of the film, i.e. evaporation instead of sputtering, does not allow the removal of the resistive silicon oxide layer always present at the surface of the substrate just before the V_2O_5 deposition, even if this substrate has been very carefully chemically cleaned.

The V_2O_5–Si junctions are therefore likely to behave as heterojunctions with a potential barrier at the interface and the silicon oxide resistive surface layer will tend to decrease the current.

The following discussion will only try to correlate the observed properties of the various junctions with the experimental parameters governing the V_2O_5 evaporation.

The results observed with Films 1 and 3 clearly establish that the V_2O_5–p-silicon junction can behave as a diode. We assume that this rectifying effect can be explained by the usual description of heterojunctions in terms of energy band diagrams, as explained in standard textbooks. Several observed features can then be interpreted in terms of the mobility of the charge carriers in the various V_2O_5 films (see Table I).

For instance the fact that illumination of Film 1 does not generate any photocurrent under reverse bias may be most readily explained by taking into account the insulating character of this form of V_2O_5 arising from the very low mobility of the charges created at the interface by illumination. Therefore, recombination of the hole–electron pairs is predominant, causing the photocurrent to be very weak. Interestingly, the photocurrent is slightly higher for Film 3 which possesses a higher mobility.

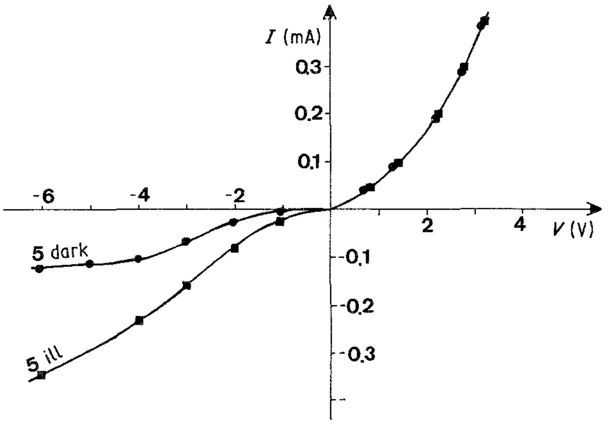

Figure 4 D.c. voltage–current characteristics of the junction using $Li_{0.1}V_2O_5$ film: (●) Film 5, no illumination; (■) Film 5 illuminated.

The main feature, common to all junction based on Films 2 and 4, is that they exhibit a very poor rectifying effect. As these films are deposited onto substrates held at 120° C, oxygen (arising from the partial decomposition of V_2O_5) is likely to form an intermediate silicon oxide film which limits the current and imposes a quasi ohmic behaviour under direct bias.

The second striking feature common to these junctions is that illumination under reverse bias generates an important photocurrent. Again, this may be tentatively explained by the higher mobility of the charges in these films (Table I), so that the electron–hole pairs generated at the interface can be separated before they recombine.

Finally, we have no satisfying explanation for the behaviour of the more complex $Li_{0.1}V_2O_5$ films.

In conclusion, this work demonstrates that amorphous V_2O_5–p-silicon junctions can act as diodes, at least under certain conditions, even though electrical conductivity in V_2O_5 occurs by means of polarons. Further work is undertaken to determine whether amorphous V_2O_5 could still generate p–n junctions with other polaronic conducting materials, especially doped conducting polymers.

Acknowledgements

The authors wish to thank B. de Cremoux and P. Poulain (Thomson C.S.F. Company, L.C.R. Corbeville, Orsay, France) for the gift of silicon wafers, for electrical measurements and stimulating discussions. They also thank C. Sanchez (Université P. et M. Curie and CNRS, Paris, France) for helpful discussions.

References

1. L. RIVOALEN, A. REVCOLESCHI, J. LIVAGE and R. COLLONGUES, *J. Non-Cryst. Solids* **21** (1976) 171.
2. N. GHARBI, M. C. LEROY, J. LIVAGE and J. P. AUDIERE, *Rev. de Chim. Min.* **18** (1981) 266.
3. K. BALI, L. MICHAILOVITS and I. HEVESI, *Acta Phys. Chem.* **25** (1979) 44.
4. T. SZÖRENYI, K. BALI and I. HEVESI, *J. Non-Cryst. Solids* **35/36** (1980) 1245.
5. J. P. AUDIERE, A. MADI and J. C. GRENET, *J. Mater. Sci.* **17** (1982) 2973.

6. L. MURAWSKI, C. GLEDEL, C. SANCHEZ, J. LIVAGE and J. P. AUDIERE, *J. Non-Cryst. Solids* **89** (1987) 98.
7. J. P. AUDIERE and A. MADI, *Thin Solid Films* **101** (1983) L29.
8. C. SANCHEZ, J. LIVAGE, J. P. AUDIERE and A. MADI, *J. Non-Cryst. Solids* **65** (1984) 285.

Received 20 May
and accepted 12 September 1988