

Diffusion of Chromium in Thin Hydrogenated Amorphous Silicon Films

© S.K. Persheyev[✉], P.R. Drapacz, M.J. Rose, A.G. Fitzgerald

Carnegie Laboratory of Physics,
Electronic Engineering and Physics Division,
University of Dundee, Dundee, DD1 4HN, Scotland, UK

(Получена 17 июля 2003 г. Принята к печати 18 июля 2003 г.)

The diffusion of chromium bottom contact has been studied through thin 10 nm amorphous silicon film. The concentration of the diffused impurity has been analysed by an X-ray photon spectroscopy technique and the diffusion coefficient was estimated. Diffusion annealing was carried out in vacuum (10^{-6} mTorr), the temperature was kept at 400°C and annealing time varied from 0–300 min. The authors propose that diffusion of chromium in thin hydrogenated amorphous film limited by silicide formation at the metal–silicon interface.

1. Introduction

While microelectronics device production is moving into nanoscale region chromium diffusion in amorphous silicon (*a*-Si:H) is a significant area of study for number of reasons. Good electrical contacts to semiconductors are crucial for the proper functioning of circuits because signals enter and leave devices through them. One requirement for contacts is chemical stability. Furthermore, it is essential that a contact does not introduce unwanted electrical characteristics such as signal rectification or high resistance into the circuit. Since *a*-Si:H consists of a random network of atoms, distorted considerably from the minimum energy sites of its crystalline counterpart, it can easily interact with other materials. Interaction at a metal/*a*-Si:H contact can cause irreversible interfacial degradation; however, it may also be used to some advantage.

Memory devices based on *a*-Si:H [1] that act as two state digital devices or analogue devices with a continuum of states depending on the nature of their metal contacts (e.g. chromium or vanadium) are finding applications as non-volatile switching materials. The nature of the top metal interaction is of crucial importance to the switching characteristics.

Amorphous silicides formed in hydrogenated amorphous silicon are not well understood despite the fact that silicides are widely used in contacting technologies for the thin film transistors needed in active matrix liquid crystal displays. The most widely studied metal is chromium, and it has been shown that silicide layers at most a few nanometres thick are formed after sputtering chromium onto hydrogenated amorphous silicon even with no subsequent annealing treatment. Recent work [2] suggests that using an ultra-thin metal-like chromium silicide in an entirely amorphous structure naturally forms a hot electron device with a high electron barrier emitter and low electron barrier collector. The aim of this work is further understanding of chromium diffusion mechanism and metal/*a*-Si:H interface reactions mediated by thermal annealing.

2. Experimental

Hydrogenated amorphous silicon layers were deposited onto Corning 7059 glass preliminarily coated with sputtered chromium as show in Fig. 1. Films were deposited using plasma enhanced chemical vapour deposition (PECVD) from silane at a substrate temperature of 300°C, applied RF power of 6.5 W, a silane flow rate 40 sccm, giving a growth rate of ~ 0.9 Å/s. Typical layers had a thickness of 10 nm for Cr diffusion experiments and 600 nm films on silicon wafers for Fourier transform infrared spectroscopy (FTIR).

Chromium was sputtered on glass substrates to a thickness of 30 nm and immediately amorphous silicon was grown to avoid Cr surface oxidation. Films for thickness measurements were patterned using an interdigital photomask and after removing the photoresist film the surface was profiled using thickness profiling technique. To study the thermal diffusion of chromium, samples on glass were annealed at 400°C in vacuum (10^{-6} mTorr) and then samples were analysed for presence of chromium in a X-ray photon spectroscopy (XPS) system. The spectra are shown in Fig. 2.

All the XPS measurements we have done were for the chromium diffusion studies using Mg-K-alpha radiation. The apparatus (a VG HB 100 adapted to incorporate XPS) was operated in constant analyser energy mode with the X-ray gun itself running at 130 W. The pass energies were 50 eV for survey scans and 20 eV for region scans. Spectra were collected using VGX900 software and the system was kept calibrated using the procedures outlined in ISO/DIS 15472.

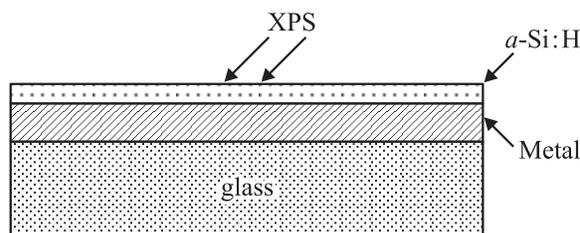


Figure 1. Schematic representation of layers for diffusion study.

[✉] E-mail: s.persheyev@dundee.ac.uk
FAX: +44-1382-348313
Tel.: +44-1382-344563

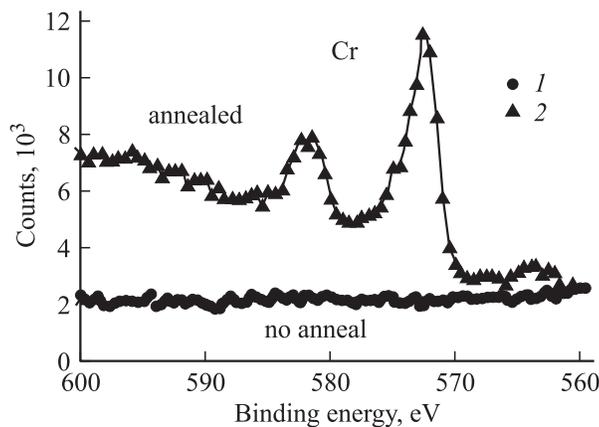


Figure 2. XPS signal from amorphous Si: 1 — before and 2 — after annealing at 400°C, 5 h.

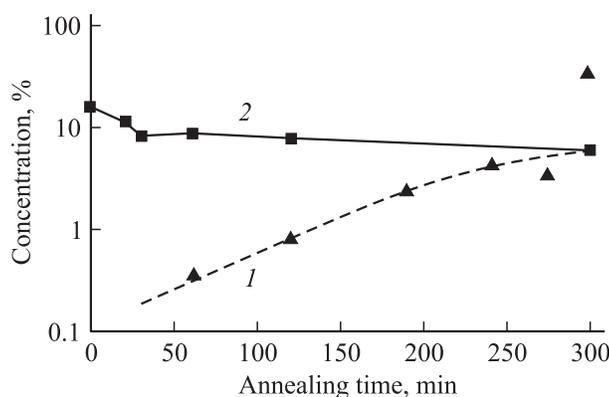


Figure 3. Concentration of chromium (1) and hydrogen (2) after annealing in vacuum. Dashed lines are our theoretical calculations for diffused chromium.

3. Discussion

The diffusion of the contact metals in PECVD amorphous hydrogenated films shows unusual behaviour of diffusing materials and is quite different than that found in crystalline silicon [3]. The diffusion coefficient of the impurity in amorphous silicon depends only weakly on the impurity itself, and the diffusion coefficient and its activation energy are nearly equal to those of hydrogen. It was found that boron diffuses quite fast with a diffusion coefficient of about 10^{-13} cm²/s and the antimony diffusion coefficient was found 10^{-14} cm²/s at 400°C. Activation energies are the same for both and are about 1.5 eV.

A. Polman and co-authors [4] studied the diffusion of copper in annealed and unannealed *a*-Si:H in the temperature range 150–270°C. The diffusion rate in annealed amorphous silicon is a factor of 2–5 times higher than in unannealed *a*-Si:H. The diffusion activation energy $E_a = 1.39$ eV in annealed *a*-Si:H is not significantly different than in unannealed *a*-Si:H, where it is measured to be $E_a = 1.25$ eV.

The diffusion of silver has been studied in previous work [5] and the authors conclude that silver diffuses in undoped amorphous silicon interstitially and through hydrogen vacancies with activation energies of 1.3 eV and 1.7 eV respectively. Interstitial diffusion described as $D_i = 4.4 \cdot 10^{-3} \exp(-1.3/kT)$ cm²/s and diffusion through vacancies as $D_v = 70 \exp(-1.7/kT)$ cm²/s.

In our experiments an annealing temperature 400°C has been chosen for two reasons: it is known that diffusion of metals in *a*-Si:H at temperatures lower than 400°C is small and requires very long diffusion annealing times, and second hydrogen effusion occurs at temperatures higher than 400°C and changes the amorphous structure and its network. The experimental results are represented in Fig. 3. As we can see from the graph the hydrogen concentration decreases from 15 to 8.3 at% mainly at the beginning of the anneal where the initial drop in the first 30 min is obviously due to hydrogen effusion from the film. At the longer times the change in the hydrogen content is relatively small and after 5 h of annealing the remaining hydrogen is about 6 at%. The change of hydrogen content in the beginning can also be explained due to relaxation processes in the amorphous matrix. With the releasing of some hydrogen we are creating additional „hydrogen vacancies“, enabling diffusion of chromium impurities. The XPS surface analysis technique allowed detection of Cr atoms diffused through the very thin 10 nm *a*-Si:H layer. The time dependence of the Cr concentration is also plotted in Fig. 3. For purpose of theoretical calculations a thick layer of Cr (30 nm) can be considered as an unlimited source, and diffusion through a thin film described as the diffusion in a body with one impermeable border [6]. The impurity concentration at the first boundary of a body ($x = 0$) has a constant value C_0 which does not change with time. The second boundary is regarded as impermeable, with $dC/dx = 0$ at $x = l$. For such a body the impurity concentration as a function of coordinate x and time t is given by

$$C(x, t) = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)} \times \exp \left[-(2k+1)^2 \frac{\pi^2}{4} \frac{Dt}{l^2} \right] \sin(2k+1) \frac{\pi}{2} \frac{x}{l} \right\}. \quad (1)$$

At the boundary $x = l$ the concentration changes with time

$$C(l, t) = C_0 \left\{ 1 - \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)} \exp \left[-(2k+1)^2 \frac{\pi^2}{4} \frac{Dt}{l^2} \right] \right\}. \quad (2)$$

After a transient period of time the terms with large k will decay away and only the first term (with $k = 0$) will have to be considered

$$C(l, t) = C_0 \left[1 - \frac{4}{\pi} \exp \left(-\frac{\pi^2}{4} \frac{Dt}{l^2} \right) \right]. \quad (3)$$

Calculation (dashed line on Fig. 3) gives a good match with the experimental results except for the last point.

Simulation results allowed to estimate of Cr diffusion in thin *a*-Si:H films with a diffusion coefficient of $4 \cdot 10^{-17}$ cm²/s, which is quite slow compared to impurities such as Cu, Sb, B and Ag. The reason is likely the processes at the silicon and metal interface. Initially, during even short deposition of *a*-Si:H on metal, Cr forms a silicide layer, which creates a barrier for the diffusion and subsequently prevents penetration of Cr atoms into the bulk. The diffusion process is followed apparently with the growth of a silicide layer, which gives a fast increase of Cr concentration at the end of the annealing ($t = 300$ min).

The same experiments were carried out using vanadium metal as the diffusion source, but even after 5 h annealing in vacuum vanadium was not found to diffuse through 10 nm thick amorphous silicon.

4. Conclusions

We have studied diffusion (at 400°C) of chromium in 10 nm *a*-Si:H films by means of XPS and found that it includes two processes. First of all silicide formation and growth during annealing at the metal–silicon interface and secondly silicide limited diffusion of Cr atoms through the thin amorphous silicon film. We propose a new XPS based method of diffusion analysis of contact materials on thin films.

The authors acknowledge R.Sh. Malkovich for helpful discussions. This work partially was supported by Royal Society NATO Advanced Fellowship.

References

- [1] J. Hu, J. Hajto, A.J. Snell, A.E. Owen, M.J. Rose. *Phil. Mag. B: Phys. Condens. Matter*, **74** (1), 37 (1996).
- [2] A. Kavsarian, J.M. Shannon, F. Cristiano. *J. Non-Cryst. Sol.*, **276**, 40 (2000).
- [3] H. Matsumura, M. Maeda, S. Furukava. *J. Non-Cryst. Sol.*, **59&60**, 517 (1983).
- [4] A. Polman, D.C. Jacobson, S. Coffa, A. Poate. *Appl. Phys. Lett.*, **57** (12), 1230 (1990).
- [5] M.S. Ablova, G.S. Kulikov, S.K. Persheyev, K.K. Khodzhaev. *Semiconductors*, **24** (11), 1208 (1990).
- [6] J. Crank. *The mathematics of diffusion* (Oxford, Clarendon Press, 1956) p. 58.

Редактор Т.А. Полянская