

OJDOS evidence for a semiconductor-to-metal transition in a-Si_{1-y}Ni_y:H

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 793

(<http://iopscience.iop.org/0953-8984/3/7/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:06

Please note that [terms and conditions apply](#).

OJDOS evidence for a semiconductor-to-metal transition in a-Si_{1-y}Ni_y:H

S C Bayliss†, R Asal‡, E A Davis‡ and T West§

† Department of Physics, Loughborough University of Technology,
Loughborough LE11 3TU, UK

‡ Department of Physics and Astronomy, University of Leicester, Leicester LE1 7RH,
UK

§ Physics and Chemistry of Solids, Cavendish Laboratory, University of Cambridge,
Cambridge CB3 0HE, UK

Received 7 June 1990, in final form 4 December 1990

Abstract. Reflectivity measurements over the energy range 0.5–12 eV have been made for the amorphous alloy system a-Si_{1-y}Ni_y:H with $y = 0.0, 0.11, 0.28, 0.45$. The infrared region of the reflectivity shows evidence of a semiconductor-to-metal transition as y is increased, whilst the visible/ultraviolet regions show a systematic shift in energy of prominent features. Using suitable extrapolations to the reflectivity data, Kramers–Kronig analysis has enabled the determination of ϵ_1 , ϵ_2 and hence the OJDOS (optical joint density of states) for the system. A schematic valence and conduction band DOS has been deduced from these data in conjunction with the previously determined variation of optical bandgap with composition.

1. Introduction

The amorphous silicon-metal alloy a-Si_{1-y}Ni_y:H has been the subject of a recent optical and electrical study [1] to investigate the nature of the semiconductor-to-metal transition as y is increased. In that study, the optical measurements were confined to the low photon energy range 0.5–2.5 eV and samples were found to be metallic for $y > 0.26$. At this value of y the optical gap E_{04} was found to have decreased to zero from 1.9 eV at $y = 0$ and the DC conductivity at room temperature to have increased to $\sim 10 \Omega^{-1} \text{cm}^{-1}$ from $10^{-5} \Omega^{-1} \text{cm}^{-1}$ for a-Si:H ($y = 0$). Reflectivity data were analysed assuming a Drude-like behaviour to obtain information on the plasma energy E_p and scattering time τ . Although the Drude model provided a very good fit to the data, the calculated optical conductivity (extrapolated to 0 eV) and the measured DC electrical conductivity showed a large discrepancy, the former being typically 150 times the latter.

We have extended the range of the reflectivity data to 12 eV in order to perform a Kramers–Kronig (KK) analysis on samples with y in the range 0 to 0.45 i.e. on samples which clearly lie on either side of the semiconductor-to-metal transition. The analysis provides information on the optical constants ϵ_1 and ϵ_2 and can be used to determine the optical joint density of states (OJDOS). Thus a clearer picture has been obtained of the changes in electronic band structure of the a-Si_{1-y}Ni_y:H system as y is varied. DC conductivity measurements on samples deposited under the same conditions as those

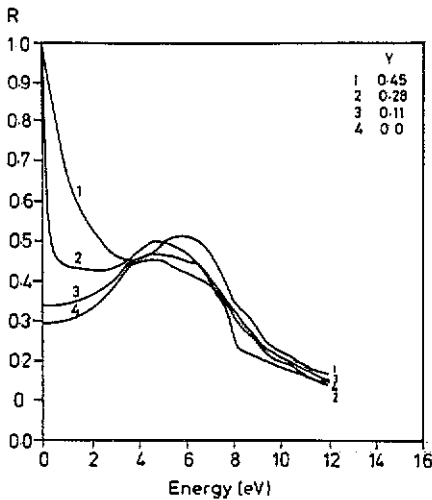


Figure 1. Reflectivity versus photon energy for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system as a function of composition (y).

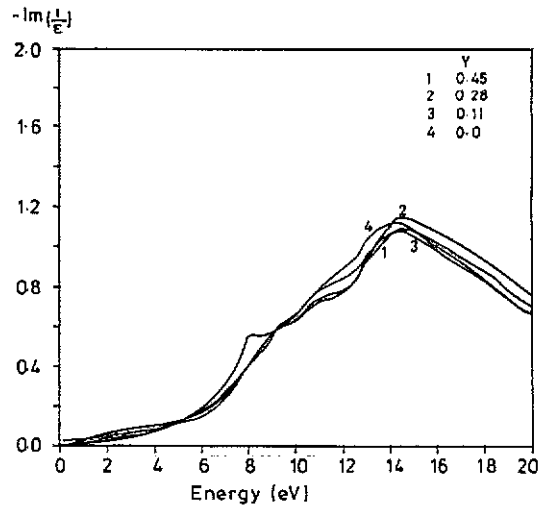


Figure 2. $-\text{Im}(1/\epsilon)$ versus energy for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system as a function of composition (y).

used for the present reflectivity measurements show good agreement with the optical conductivity calculated from the derived ϵ_2 data.

2. Experimental details

A series of relatively thick films ($>2 \mu\text{m}$) of $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ were prepared for reflectivity measurements by the technique of RF sputtering in an argon/hydrogen atmosphere. The targets were wafers of silicon on which were placed appropriate amounts of nickel. The substrates of Corning 7059 glass were maintained at room temperature. The compositions of the films were obtained by x-ray fluorescence spectroscopy in a SEM giving an accuracy in y of ± 0.02 . The samples were shown to be amorphous by TEM studies.

The near-infrared and visible reflectivity measurements (0.5 to 4.5 eV) were carried out using a Perkin Elmer 330 spectrophotometer in the Physics Department at Leicester whilst visible and vacuum ultraviolet (VUV) reflectivity measurements (1.5 to 12 eV) were made using a purpose built spectrometer at the Cavendish Laboratory, Cambridge. Details of the latter instrument can be found in [2]. The reflectivity data from the two instruments were found to be in good relative agreement in the overlap region and the datasets were matched absolutely at 3.5 eV. This required scaling factors of ~ 1.1 to be applied to the VUV data. The reflectivity spectra obtained for this system for values of y from 0.0 to 0.45 are shown in figure 1.

There is clear evidence of Drude-like behaviour (free-carrier intraband transitions) for $y > 0.26$ from the sharp rise in reflectivity at low energies (figure 1). For lower values of y the low-energy reflectivity shows behaviour consistent with the existence of a classical oscillator centred at higher energies i.e. typical of an insulator or semiconductor. At higher energies this behaviour is seen for all values of y as a large broad peak centred around 4–6 eV. With increase in y there is a monotonic increase in strength and a notable shift in position of this feature for $y = 0.45$. Closer inspection reveals that this feature

can be resolved into two—a peak followed by a shoulder about 2 eV higher in energy, presumably due to features in the valence band (VB) or conduction band (CB) DOS. It is possible that the increase in strength of these features with y is due to a change in core polarization, rather than to changes in the DOS or transition matrix elements.

At higher energies the spectra for all values of y are very similar in shape. The feature around 8 eV for $y = 0.11$ is thought to be an anomaly of the particular sample and not representative of the system.

In order to perform KK analysis on the reflectivity spectra the data have to be extended to cover in principle an infinite energy range. In practice this requires that the dataset be extrapolated to low (i.e. zero) and high energies. This has been done by smoothly extending the low energy data to a reflectivity of unity for the metallic samples and to a zero value of dR/dE for the semiconducting samples at $E = 0$. At the high energy end the data have been extrapolated to 100 eV assuming $R(E) = R_t (E_t/E)^4$ where R_t is the reflectivity at the highest energy measured E_t . Discussion of appropriate extrapolations can be found in many standard texts such as Wooten [3].

The variation of $\theta(E)$ with E is obtained from the dispersion equation

$$\theta(E) = -\frac{E}{\pi} \int_0^\infty \frac{\ln(R(E')/R(E)) dE'}{(E'^2 - E^2)} \quad (1)$$

The optical parameters n , k , ϵ_1 and ϵ_2 can be found from the equations

$$n(E) = (1 - R(E))/[1 + R(E) - 2(R(E))^{1/2} \cos \theta(E)] \quad (2)$$

$$k(E) = 2(R(E))^{1/2} \sin \theta(E)/[1 + R(E) - 2(R(E))^{1/2} \cos \theta(E)] \quad (3)$$

$$\epsilon_1 = n^2 - k^2 \quad (4)$$

$$\epsilon_2 = 2nk \quad (5)$$

From ϵ_2 the OJDOS is obtained via

$$\text{OJDOS} = C E \epsilon_2 \text{ states eV}^{-1} \text{ per } \text{Si}_{1-y}\text{Ni}_y\text{:H formula unit} \quad (6)$$

where C is a constant depending on atomic density and the matrix element (taken here to be unity throughout the whole energy range).

A sum rule can be used to estimate the effective number of electrons per formula unit n_{eff} contributing to the optical constants up to an energy E_c (see for example [3]).

$$\int_0^{E_c} E \epsilon_2(E) dE = E_p n_{\text{eff}} \quad (7)$$

where E_p is the plasma energy $\hbar\omega_p$ for electrons involved in both inter- and intra-band transitions. Since there is not much change in the main interband region of the reflectivity spectra as a function of composition, E_p cannot change very much with composition. This is supported by loss function data:

$$-\text{Im}(1/\epsilon) = (\epsilon_2/|\epsilon|^2) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2) \quad (8)$$

since the rate of energy absorption per unit volume dE_A/dt is given by

$$dE_A/dt = \omega \epsilon_2 |E|^2 = \omega \epsilon_2 |D|^2 / |\epsilon|^2 \quad (9)$$

for an electric field E incident on the material. Here D is the field which would be produced in the solid by an impinging electron. The factor $\epsilon_2/|\epsilon|^2$ rises rapidly and peaks

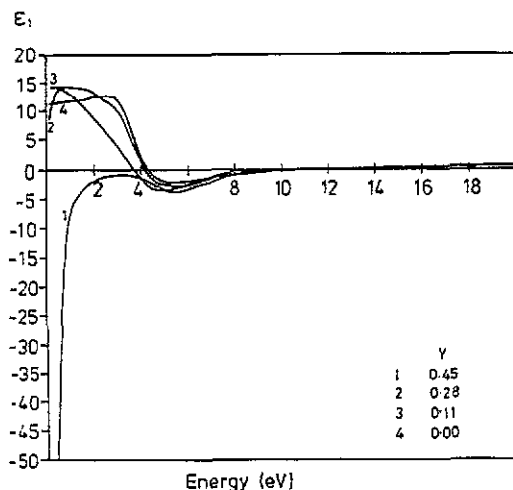


Figure 3. ϵ_1 versus energy (eV) for the a-Si $_{1-y}$ Ni $_y$:H system as a function of composition (y).

around the plasma energy i.e. in the region of plasmon excitation. For the case of a-Si:H we find the peak of $-\text{Im}(1/\epsilon)$ occurs at ~ 14 eV (figure 2) whereas a value of 16.7 eV for E_p is generally accepted [4]. We believe this discrepancy arises from small errors in data extrapolation. Here we use the function $-\text{Im}(1/\epsilon)$ to predict changes in E_p with y rather than to obtain absolute values of E_p . We find that the peak energy of $-\text{Im}(1/\epsilon)$ increases to 14.5 eV with $y = 0.45$, reflecting the increase in n_{eff} with y shown in figure 6. In the above calculations therefore we have taken E_p to vary monotonically from 16.7 eV for $y = 0$ to 17.2 eV for $y = 0.45$.

3. Discussion

The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant obtained from the analysis described above are shown in figures 3 and 4 respectively. It should be noted that the behaviour of ϵ_1 and ϵ_2 is extremely sensitive to small changes in the extrapolated reflectivity data. A linear extrapolation below 0.5 eV yielded anomalous results for one sample ($y = 0.28$) and a gradient matched extrapolation was used instead.

It can be seen from figure 3 that ϵ_1 shows a gradual change as a function of y from the behaviour expected of an insulator (for $y < 0.26$) to that expected of a metal (for $y = 0.45$). Metallic character manifests itself as a large negative ϵ_1 which tends to zero in the low energy region of figure 3. This is associated with plasma oscillations of free electrons (giving rise to intraband transitions) and should be distinguished from the VB plasma energy which is in addition associated with bound electrons (giving rise to interband transitions).

With increasing y the plasma energy for interband transitions (which occurs when $\epsilon_1 \rightarrow 0$ from below), does not change appreciably, supporting the assumption that the plasma energy is virtually constant. For $y = 0$ and 0.11, ϵ_2 (figure 4) shows behaviour typical of a single classical oscillator centred just below 4 eV. Increasing y leads to an increase in DOS at low energies, corresponding to a reduction in the energy gap. Beyond $y = 0.28$, the conduction and valence bands overlap and metallic behaviour occurs.

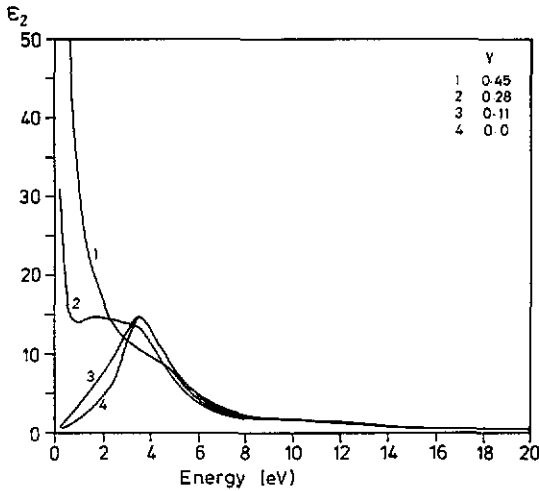


Figure 4. $-\text{Im}(1/\epsilon)$ versus energy (eV) for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system.

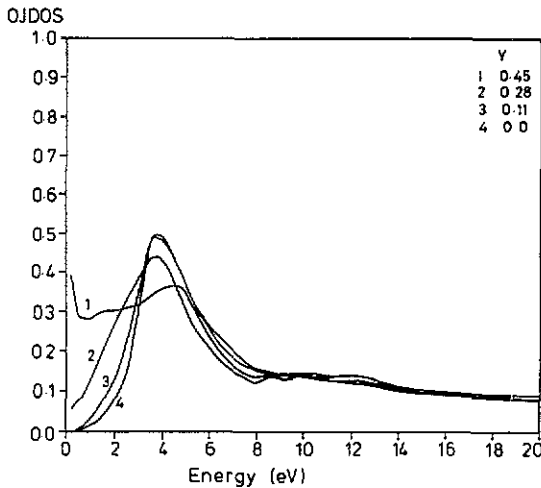


Figure 5. OJDOS states $(\text{eV})^{-1}$ per $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ formula unit versus energy for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system as a function of composition (y) assuming a constant atomic density of $5 \times 10^{22} \text{ cm}^{-3}$.

For $y = 0.45$ there is an increase in strength of this behaviour relative to $y = 0.28$, corresponding to an increase in plasma energy for the intraband transitions. This is equivalent to an increase in the number of electrons involved since $E_p \propto (n_{\text{eff}})^{1/2}$.

The OJDOS spectra (figure 5) basically reflect the ϵ_2 spectra. However, the features are more pronounced and it is possible to identify the position and movement of the two main interband features observed in the reflectivity shown in figure 1. Whereas the shifts are of the same value in figures 1 and 5 for a particular value of y , the absolute positions of the OJDOS features are seen to be at least 1 eV below the corresponding features in the reflectivity spectra. It should be noted that the OJDOS for $y = 0.28$ is just above zero at 0 eV confirming the existence of a band overlap.

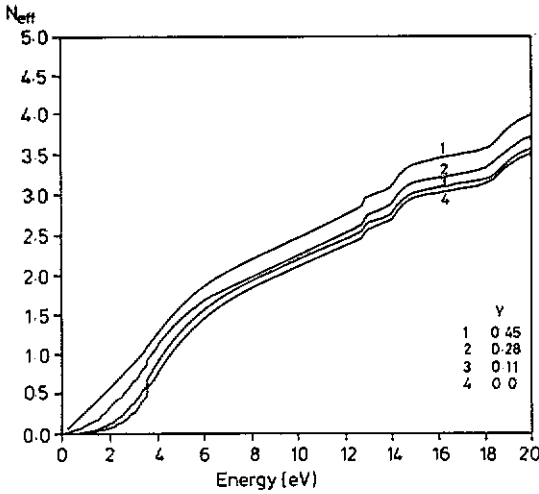


Figure 6. N_{eff} per $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ formula unit versus energy (eV) for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system as a function of composition (y) assuming a constant atomic density of $5 \times 10^{22} \text{ cm}^{-3}$.

The values of n_{eff} shown in figure 6 have been calculated assuming a constant atomic density of $5 \times 10^{22} \text{ cm}^{-3}$. This is justified since $E_p^2 = (e^2/\epsilon_0 m)N_v$, where N_v is the density of valence electrons, and we have seen that E_p is approximately constant. Now

$$N_v = \{[(1 - y)n_{\text{Si}} + yn_{\text{Ni}}]/[(1 - y)A_{\text{Si}} + yA_{\text{Ni}}]\}\rho L_A$$

where A_{Si} and A_{Ni} are the atomic weights in g of silicon (=28) and nickel (=59) respectively, n_{Si} and n_{Ni} are the number of valence electrons of silicon (=4) and nickel (=2) respectively, L_A is Avogadro's Number, ρ is the density (g cm^{-3}). Little change in density is thus found with change in y (assuming N_v constant): for example assuming $\rho_{(y=0)} = 2.3 \text{ g cm}^{-3}$, $\rho_{(y=0.5)} = 2.2 \text{ g cm}^{-3}$. It can be seen that by 1 eV, well below the expected onset of interband transitions, there is approximately 1/4 electron contributing to intraband transitions for $y = 0.45$, a differential maintained throughout the energy range. That the appropriate differential is not maintained fully for $y = 0.28$ reflects the presence of the spurious dip at about 8 eV in the reflectivity for this sample (figure 1).

Consideration of the above has led to the schematic diagram shown in figure 7 for the electronic band structure as a function of composition. The occupied electron states (VB) denoted by shading in figure 7 are separated from the unoccupied states (CB) by an energy gap which decreases as y is increased. In our schematic model this gap has been fixed by consideration of the Tauc gap appropriate for these materials [1]. For $y = 0.45$ when the material is metallic there is a high degree of overlap of the VB and CB and the resulting Fermi level E_F is shown. The composition of the DOS will now be discussed in detail. For $y = 0.0$ i.e. $a\text{-Si}(\text{:H})$ in the region from 0 to -5 eV, the VB consists of Si 3p levels and the CB is composed of Si 3p* antibonding levels. As nickel is introduced ($y = 0.11$) the top of the VB is replaced by Ni 3d levels which are higher in energy than the Si 3p levels. The corresponding Ni 3d* antibonding levels are probably located at the bottom of the CB. This gives rise to an increase in OJDOS between 1 and 2 eV (figure 5). (It should be noted that there will be some mixing of the bands so the assignments given

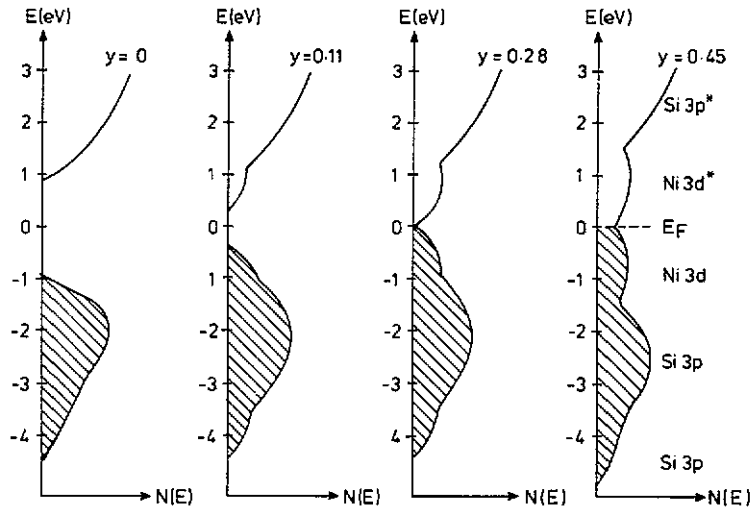


Figure 7. Schematic density of states $N(E)$ versus binding energy E (eV) for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system as a function of composition y . Filled states shown shaded.

here are those of the major component. Also, the total relative areas of the VB–CB DOS in figure 7 are based on the values of n_{eff} at the plasma energy.)

As the relative amount of nickel increases this low energy DOS contribution strengthens and broadens until a VB–CB overlap occurs at $y = 0.28$. For increasing y the overlap increases and metallic behaviour occurs. At higher energies the optical properties show an increase in the energy of the main $\text{Si } 3p \rightarrow 3p^*$ transitions with increase in y , indicating a shift down in energy of the $\text{Si } 3p$ levels in the VB and a corresponding increase in energy of the $\text{Si } 3p^*$ levels in the CB.

Values of the optical conductivity calculated from this data are of the same order of magnitude as those obtained from the limited-range optical data presented previously [1]. Theye *et al* [5] found virtually no discrepancy between the calculated optical conductivity and the measured DC electrical conductivity for the similar systems $a\text{-GeAu}$ and $a\text{-GeAg}$ and their values of σ_{DC} approach those determined for $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ from optical data. This suggests the possibility that the conductivity data of Davis *et al* [1] and also of Rogachev *et al* [6] are anomalously low, perhaps because in their samples conduction occurred via narrow percolation channels.

4. Conclusions

We have performed Kramers–Kronig analysis on reflectivity data to obtain optical constants as a function of energy and composition for the $a\text{-Si}_{1-y}\text{Ni}_y\text{:H}$ system. OJDOS data have been used to suggest a schematic CB–VB DOS which is fitted to optical gap data. Clear DOS evidence for a semiconductor-to-metal transition with increase in y is obtained from the OJDOS data.

Acknowledgments

SCB wishes to thank the SERC for the award of a postdoctoral research assistantship. R Asal thanks the Ministry of Higher Education in Iraq for financial support. The work was made possible by grants from the SERC.

References

- [1] Davis E A, Bayliss S C, Asal R and Manssor M 1989 *J. Non-Cryst. Solids* **114** 465
- [2] Shen T 1987 *PhD Thesis* University of Caambridge
- [3] Wooten F 1972 *Optical Properties of Solids* (New York: Academic)
- [4] Karcher R, Ley L and Johnson R L 1984 *Phys. Rev. B* **30** 1896
- [5] Theye M L, Nguyen Van V and Fisson S 1983 *Phil. Mag. B* **47** 31
- [6] Rogachev N A, Smid V, Mares J J and Kristofik J 1987 *J. Non-Cryst. Solids* **97** and **98** 955