

Hydrogen Absorption and Electronic Property Change of Yttrium Thin Films

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Yttrium thin film, 580nm thick, was prepared by electron beam evaporation. Film was hydrogenated at room temperature upto 40 bar hydrogen pressure, without any activation process. Hydrogen concentration was determined by a quartz-crystal microbalance(QCM) method. YH_{2.9} sample was made without any pulverization. Electrical resistance was measured by four-point DC method in the temperature range between room temperature and 30K for various hydrogen concentration, x=0 to 2.9 of YH_x sample. Temperature dependent resistance of YH_{2.9} shows low temperature minimum at 105K, the metal-semiconductor transition at 260K, and a hysteresis above 210K.

1. INTRODUCTION

Metal-hydrogen system exhibits various interesting phenomena which do not show up in host metal. Many researchers pay attention to this system on theoretical and technological aspects. The hydrogen atoms and vacancies on the interstitial sites provide a physical model of a lattice gas, the hydrogen atoms and vacancies provide a model of a binary alloy, and the occupied and unoccupied interstitial sites are analogous to the Ising model of antiferro-

magnetism. On the technological sides of metal-hydrogen system are hydrogen storage, hydrogen isotope separation, hydrogen induced embrittlement, and hydrogen induced amorphization. Recently, physicists predict superconductivity at about 230K in metal phase of atomic hydrogen at very high pressures(3×10^8 bar).^[1-5] It was suggested that we would have superconducting under about 1×10^8 bar pressure if small amount of yttrium, lanthanum, and possibly barium is dissolved in sufficient quantities of hydrogen.^[6] It is well-known that

the early transition metals(e.g. Y and La) and some of the rare-earths can form trihydrides, which possibly satisfy the above requirement for superconducting. These systems are also interesting since that the metal-to-semiconductor(M-S) transition is observed in some composition range near MeH_3 (Me=3B-subgroup elements).^[7]

Electrical property measurements under high pressure are usually done in high pressure diamond envil cell with sample shape as thin film because of limitation of the diamond envil cell size. Sample for resistivity measurement will be made on surface of diamond. For the introductory experiment, we tried to make yttrium thin film on sapphire substrate at room temperature, load hydrogen gas into Y film and measure temperature dependence of resistivity of $\text{Y}(\text{H}_x)$ system in the temperature range between room temperature and 30K under 1 bar pressure. The optical and acoustic electronphonon coupling in YH_x system is examined by using Bloch-Grüneisen and Einstein formula of resistivity of metal-hydrogen system.^[8]

The amount of absorbed hydrogen on yttrium film on the diamond at various hydrogen pressure is not known yet. The amount of hydrogen absorbed in the yttrium film can be monitored by using a quartz crystal thickness monitor^[9] at room temperature. Thus yttrium film was evaporated on 6 MHz quartz crystal for hydrogen absorption-desorption study. Hydrogen is loaded upto 40 bar at room temperature. Temperature and pressure calibration of quartz crystal resonant frequency

data were used to deduce real frequency change due to hydrogen absorption.

2. EXPERIMENTS

Thin film Y samples were made with 99.9% purity Y(from Leico Industries, Inc) on 6 MHz AT cut quartz crystal(crystal diameter=14 mm, Y film diameter=7mm) for QCM measurements, and on sapphire substrate for resistivity measurements. Y film was evaporated on substrate by electron beam under working pressure 8×10^{-8} torr(distance between E-beam source and substrate is about 40cm, substrate temperature is room temperature, and evaporation speed is 0.5nm/sec). The film on sapphire substrate is cutted into about 1 mm x 10 mm shape by tungsten carbide needle for the four-point DC resistivity measurement. The sample was mounted on sample holder for resistivity measurements in continuous flow cryostat without loading hydrogen. Cooling rate and warming rate of the sample are about 12K/min. and 2K/min. respectively. Table 1 shows charac-

Table 1 Characteristics of thin film Y samples

| Sample name | Y 1.2 | Y 1.6 | Y 2.3 | Y 3.1 | Y 4.1 | Y 5 |
|---|---|-------|-------|-------|-------|------|
| Film Thickness(nm) | 580 | 580 | 580 | 580 | 580 | 588 |
| Residual resistivity($\mu\Omega$ cm) | 116 | 116 | 97 | 73 | 132 | 81 |
| Resistivity ratio, ρ_{300K} / ρ_T | 1.64 | 1.64 | 1.79 | 2.24 | 1.88 | 2.15 |
| Sample Y6, Y21+, and Y22 | samples for QCM measurements(thickness=580nm) | | | | | |

* gold film on quartz crystal was etched away before Y evaporation.

teristics of several Y film samples. Average of resistivity ratio of the above samples was about 1.9, which is rather bigger than bulk. Difference may be due to the dimensions of thin film and/or impurities in film.

Experimental set up can be seen in Fig. 1. Temperature of the sample was

measured with PT-100 thermocouple. Temperature of the sample and all of the electric parts were changed with room temperature change for QCM measurement. It is known that the resonant frequency of the crystal changes with the changes of the pressure⁽¹⁰⁾ and temperature⁽¹¹⁾ of the gas surrounding the crystal. Thus gas pressure calibration was done with high purity helium and hydrogen gas at room temperature upto 40 bar. Frequency shifted about 206 Hz to the high-frequency side with 40 bar hydrogen gas while frequency shifted 166 Hz with helium gas. Thus all of the

following analysis we used hydrogen calibration data. We assumed that frequency change with thin film on crystal is same as frequency change without film on it. There was no difference in frequency change when we compare frequency change with helium gas with Y film on crystal and without film on it.

Hydrogen gas(99.999% pure) was introduced into the sample chamber at room temperature. Hydrogen pressure was increased step by step to reduce sudden change of the sample temperature due to hydrogen absorption, which could cause permanent damage to the sample. Hydrogen pressure was monitored by Viatron Model 104 pressure transducer with Viatron model 1109 strain gauge conditioner/indicator. Crystal resonant frequency was measured with Philips model PM 6673(10 Hz to 120 MHz range, resolution 0.1Hz).

The resistivity of the sample was measured by fourpoint DC method during hydrogenation. When the resistivity of the sample(sample Y 3.1) was changed to the desired value, the sample was cooled and warmed to measure the temperature dependence of resistivity. After this measurement hydrogen was loaded more into the sample and do the same experiments over. One of the samples(sample Y 3.1) was examined the hydrogen absorption and desorption cycling effect.

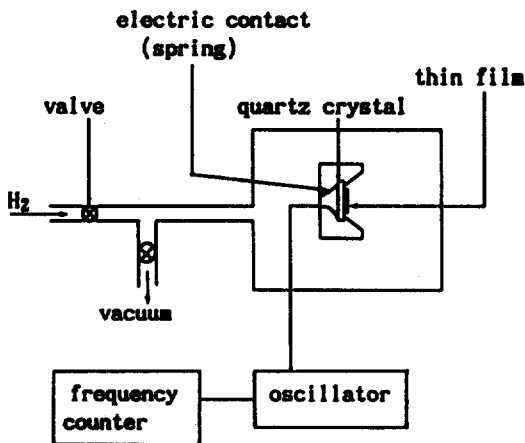


Fig. 1 Schematic diagram of the quartz-crystal microbalance(QCM).

3. RESULTS AND DISCUSSIONS

1. Hydrogen absorption measurement by QCM method

Fig. 2 shows quartz crystal resonant frequency change of sample Y 21 with increasing hydrogen pressure step by step at room temperature. No activation process was needed for hydrogenation. In contrast to bulk, which is completely powdered at [H/Y]=3, Y film was not powdered during the experiments.

Change of frequency is roughly proportional to the change of hydrogen concentration in Y film. One can see two regions in Fig. 2. Part A and C in Fig. 2 show similar behavior to each other. Ratio of frequency change to time is

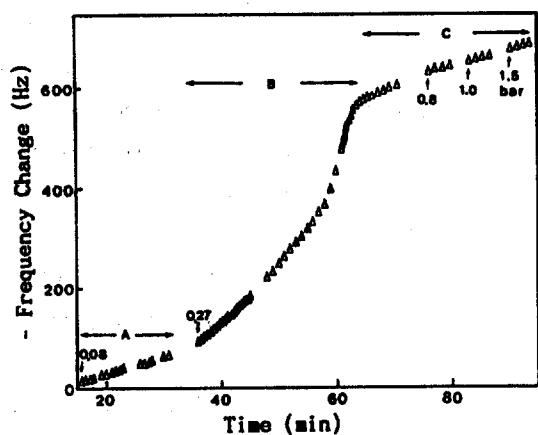


Fig. 2 Change of crystal resonant frequency during hydrogen absorption on 580 nm thick yttrium film at room temperature (reference frequency=5965.6971KHz).

about 0.054Hz/sec for part A and 0.062Hz/sec for part C. In contrast to these parts, frequency changes rapidly with time in part B. Part A, B, and C would be corresponding to α -phase, mixed phase, and hydride phase, respectively.

[12,13] We could not wait until resonant frequency

reaches to the saturated value, because sample temperature changes(due to change of room temperature) if we wait too long at the fixed hydrogen pressure. For more reliable analysis on hydriding YHx film, we need very stabilized temperature controlled experimental set ups.

Hydrogen concentration in YHx sample was calculated by using following equation^[9]

$$\Delta m = 4.417 \times 10^5 (1/f_f - 1/f_q),$$

where Δm is measured in g/cm^2 and the frequencies are gauged in Herz. f_q is the resonant frequency before hydriding and f_f is the resonant frequency after hydriding. Figure 3 shows hydrogen concentration vs. hydrogen pressure. As pointed above, the hydrogen concentration is not equilibrium value during hydrogen absorption. One can see that the concentration at 5 bar is more than 300%, which is higher than what we expect. This might be due to error in resonant frequency,

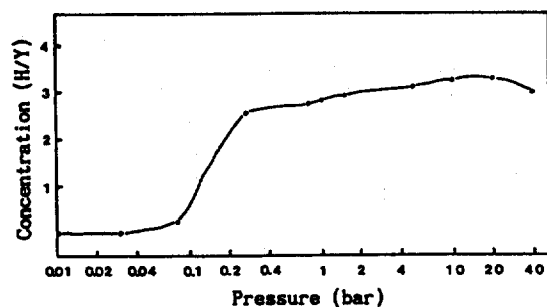


Fig. 3 Hydrogen concentration change vs. hydrogen gas pressure in yttrium film(580 nm thick sample Y 21) at room temperature during hydrogen absorption.

thickness measurements of film, and/or stress effect(due to hydrogen absorption) in hydride sample. More systematic experiments on this problem is carried on.

Part of the hydrogen was evacuated when the sample chamber was pumped out at room temperature. Hydrogen concentration reduced to about 90% of the maximum value when the sample(sample Y 21) was in vacuum several hours. Hydrogen was loaded again into the sample after first absorption-desorption. At 0.8 bar pressure, hydrogen concentration is almost saturated to the maximum value. It is possible to remove part of the hydrogen from the sample easily and also add hydrogen to sample at room temperature.

Almost same experiments were done on sample Y 6 and Y 22. Those exhibit very similar behavior as sample Y 21, even though sample Y 21 has different substrate from other samples (i.e. gold film was etched away before Y evaporation. This was done to see the effect on hydrogen absorption due to difference in substrate layers.)

2. Electronic property change

Fig. 4 shows change of resistivity of Y 2.3 sample during hydrogenation at room temperature. In the beginning, the resistance increases gradually and reaches the peak and decreases down to minimum. After this minimum, resistance increases enormously($R/R_0=17.5$, R_0 =resistance of Y). This rapid increasing of resistance indicates M-S transition, as other S-B subgroup metal-

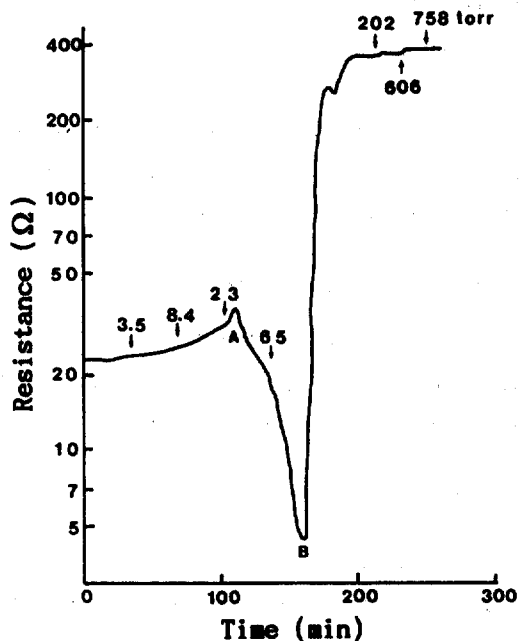


Fig. 4 Resistance variation during hydrogen charging to 580 nm thick(0.64mm x 5.5mm) yttrium sample(sample Y 2.3) at room temperature(pressure in figure is equilibrium hydrogen pressure in torr).

hydrogen system. Typical time duration for the equilibrium of hydrogen concentration was about 10 min. at room temperature. Hydrogenation of Y foil(0.2mm thick) was done at 550-600°C for dihydride and at 250-300°C for YH_{2+x} , $x=0.10$.^[14]

It is known that M-S transition occurs at $x=2.8\sim 3.0$. Concentration of H in YH_x was not measured directly, but x would be greater than 2.8 because of M-S transition shown in our samples. Resistance of YH_x reduced to the 61% of the maximum value when the sample(sample Y 2.3) was in vacuum about 70 hours at room

temperature. When this film was loaded with hydrogen gas again, it is very easy to reach the maximum resistance value.

The temperature-dependent part of the electrical resistivity, $\rho(T)$ can be expressed by Bloch-Grüneisen formula as follows,^[8]

$$\rho(T) = c(T/\theta)^5 \int_0^{\theta/T} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})}, \quad (1)$$

where θ is Debye temperature, T is absolute temperature. Eq.(1) goes over at high enough temperature into the linear relation

$$\rho(t) = A^{ac} T, \quad (2)$$

where A^{ac} is constant.

For rareearth hydride case, one can split the phonon spectrum into an acoustic part with a cut-off given by the Debye temperature θ_D of the host metal (with $\theta_D \sim 100-300K$), and a well separated optical part due to the H(or D) vibration, which can be expressed by a Einstein temperature ($\theta_E(H,D) \sim 1000-1500K$). One can rewrite Eq. (1) as follows,

$$\rho(T) = \rho^{ac}(T) + \rho^{op}(T) \quad (3)$$

At low temperature, only acoustic phonons are excited. $\rho(T)$ would be $\rho^{ac}(T)$. It is possible to determine A^{ac} and θ_D from experimental data. At higher temperatures, acoustic and optical phonons are both excited. Thus it is possible to separate resistivity due to optical phonon excitation if $\rho^{ac}(T)$ is known.

Figure 5 and 6 show temperature dependance of resistivity of thin film YH_x samples. Experimental data in Fig. 5 were obtained as follows. When resistance reached first peak (i.e.

point A in Fig. 4 during hydrogenation, hydrogenation was stopped and the sample was cooled and warmed for $\rho(T)$ measurements. One can observe a very weak hysteresis between 150K and 220K (not shown in here), and a kink at about 177K, which is pretty same as that the low temperature transition exhibited in the solid solution phase of $YH_{0.15}$.^[15] The increase of curvature above 170K indicates the contribution of the optical phonons, due to conduction-electron scattering by the vibrations of the hydrogen.^[14]

Solid line in Fig. 5 shows typical curve fitting to the experimental data by using Eq. (1). Fitting program adjusts C, θ and

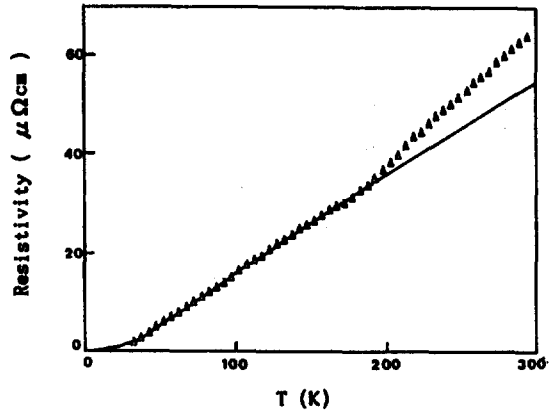


Fig. 5 Temperature dependence of the resistivity of 580 nm thick YH_x sample (sample Y 3.1). Background was subtracted from experimental data for comparison with calculated value (solid line is calculated value with $c=152 \mu\Omega$ cm, $\theta_D=175K$, and background= $21 \mu\Omega$ cm in Eq. (1))

background(ρ_{impurity}) for best fitting in the temperature range 0 to 140 K.^[8](Fitting parameters are in figure caption.) Same kind of $\rho(T)$ measurement was done, when the resistance of the sample reached first minimum (point B in Fig. 4) during subsequent hydriding process. This measurement exhibit similar temperature dependence with Fig. 5. Fitting parameters are a little different from previous data, i.e. $C=184\mu\Omega\text{cm}$, $\theta_D=283\text{K}$, and background= $48.0\mu\Omega\text{cm}$ in Eq. (1), $A^{\text{ac}}=0.162\mu\Omega\text{cm/K}$ in Eq. (2). The trend of the change of Debye temperature of our film samples is similar to the bulk sample($\theta_D(\text{Y})=210\text{K}$, $\theta_D(\text{YH}_2)=340\text{K}$ ^[8]), but the magnitude is about 80 % of the bulk value.

Optical phonon spectrum can be approximated by an Einstein delta function located at an energy^[8]

$$\rho^{\text{op}}(T)=A^{\text{op}}\theta E(H) f(X_H), \quad (4)$$

where $f(X_H)=X_H/((e^{X_H}-1)(1-e^{-X_H}))$, $X_H=\theta E(H)/T$ and $\theta_E(H)=1475\text{K}$. Optical resistivity can be obtained by using Eq.(3), e.g. $\rho^{\text{op}}(T)=\rho(T)-\rho^{\text{ac}}(T)$. $\rho^{\text{ac}}(T)$ was calculated with fitting parameters which were determined by using low temperature range($T<140\text{K}$) experimental data. In fact the difference $\rho(T)-\rho^{\text{ac}}(T)$ is sensitive to the choice of C and θ_D . But it was certain that there is definite deviation between experimental data and calculated acoustical resistance above 150K(Fig. 5). Calculated $\rho_{\text{op}}(T)$ data were used to obtain fitting parameter A^{op} . Best fitting of A^{op} for data from Fig. 5 is $0.365\mu\Omega\text{cm/K}$.

Fig. 6 shows temperature dependence, of resistivity of sample Y 5($\text{YH}_x=2.9$). This sample exhibits, i) at low temperature, there is minimum at 105K($42\mu\Omega\text{cm}$ deep), ii) the M-S transition at 260K, and iii) a big hysteresis above 210K. The above features were also observed in $\text{YH}_{2.095}$ bulk sample.^[14]

An Arrhenius graph of the temperature dependence the above sample is shown in Fig. 7 to obtain an effective activation energy E_a .^[14] Resistivity can be written as $\rho=\rho_0 \exp(E_a/kT)$. Table 3 shows the comparison of several parameters of our data to Daou's work.^[14] Eventhough each parameter is not same to each other, general trend is pretty similar. Discrepancy between two samples maybe due to hydrogen concentration difference and/or thickness of samples. More experimental data are needed for systematic analysis.

4. CONCLUSION

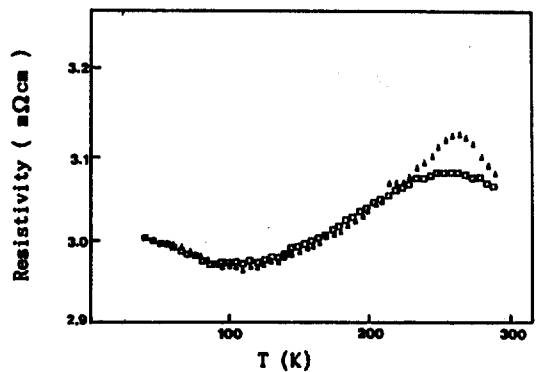


Fig. 6 Electrical resistivity of 588 nm thick $\text{YH}_{2.9}$ (sample Y 5). \square :data of cooling run and \blacktriangle : data of warming run.

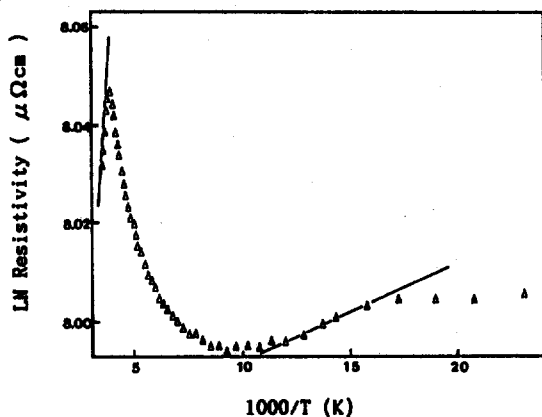


Fig. 7 Arrhenius graph for 588 nm thick YH_{2.9} specimen (sample Y 5). Effective activation energy was determined by the solid lines for low temperature side and high temperature side.

Thin film Y specimens (580 nm thick) were hydrogenated at room temperature without any activation processes. Maximum hydrogen concentration was about 290 at.% with 40 bar hydrogen gas pressure, but most of hydrogen

Table 3 Comparison of characteristics of our sample and bulk sample

| Sample | low temperature minimum | | M-S transition temperature | E _a (meV) | |
|-----------------------|-------------------------|--------------------------|----------------------------|----------------------|------|
| | T _{min} | depth | | LTc | HTc |
| YH _{2.9} a | 105 K | 42 $\mu\Omega\text{cm}$ | 260 K | 0.163 | 4.96 |
| YH _{2.085} b | 40 K | 2.1 $\mu\Omega\text{cm}$ | 284 K | 0.14 | 18 |

a : our work on 588 nm thick Y film which was loaded with 1 atm hydrogen gas.

b : warming data of quenched bulk sample.[14]

c : LT = activation energy of low temperature side,

HT = activation energy of high temperature side.

was loaded at rather low pressure (about 1 bar). Only small part of absorbed hydrogen can be removed by pumping at room temperature. Temperature dependence of YH_{2.9} exhibits low temperature minimum at 105 K, metal-to-semiconductor transition at 260 K, and a hysteresis above 210 K, which are very similar to bulk specimen.^[14] Several discrepancies are observed in characteristics between film and bulk, but the origin of these is not clear yet. More systematic investigations, such as in situ or simultaneous measurements of QCM and resistivity measurements^[16] of YH_x film specimen will be needed for better understanding.

Acknowledgements

Authors thank Prof. dr. R. Griessen and H. Huiberts for a valuable discussion, J. Rector for sample preparation, K. Heeck and Myoung-sook Won for computer program. This work was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1991.

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