

Similarity of electronic structure and optical properties of Mg_2NiH_4 and Si

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Using the first-principles calculations comparative analysis of electronic structure and optical properties of crystalline Si with cubic Mg_2NiH_4 and monoclinic Mg_2NiH_4 have been performed. It is found that band structure of cubic Mg_2NiH_3 is similar to that of crystalline Si (*c*-Si), whereas the band gap of monoclinic Mg_2NiH_4 is similar to that of hydrogenated amorphous Si (*a*-Si:H). It is shown that cubic Mg_2NiH_4 posses the features of semiconductors such as wide fundamental band gap, capability for *n*- and/or *p*-type electrical conductivity, and small carrier effective masses. It is concluded that Mg_2NiH_4 can be considered as a candidate, which is capable to replace *c*-Si and *a*-Si:H. It might be useful for processing of electronic devices such as, e.g., solar cells at low temperatures. Advantages of using hydrides in semiconductor electronics are discussed.

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Si is one of the widely used elements of modern semiconductor electronics and photovoltaics (PV). More than 90 percent of the solar infrastructure is based on 300 μm thick wafers of crystalline Si, which are sliced, processed into cells, and then connected to modules. However, during the processing about 50% of Si is lost as sawdust. In order to have sufficient mechanical strength sometimes, the wafers are also sliced much thicker than needed. As a result the Si wafers form more than half of the cost of the completed module. Because of these reasons Si based solar cells still remain to be relatively expensive, which limits their penetration into the market. In this sense search of alternative low-cost materials with low-cost processing, with at least the same electronic structure, electrical, and optical properties as crystalline Si is one of the important problems to reduce cost of the PV cells at least to a level comparable with fossil fuels.

Often, the Si based devices are doped by H to passivate defects and to improve its electrical properties.¹ This approach also meets certain technological difficulties. One of them is related to low solubility limit of H in Si $\leq 10^6$ at/cm³ at 400 °C.² At doping levels higher than this limit, structural defects can be formed, Si can lose its crystallinity,³⁻⁵ and can be converted to hydrogenated amorphous (*a*) Si (*a*-Si:H). Nowadays, the latter forms the basis of “Giant Microelectronics”.⁶ However, electrical conductivity of *a*-Si:H is known to be poorer than its crystalline counterpart and search of alternative material with more superior electrical, optical, and passivating properties than *a*-Si:H is another important problem of the modern semiconductor electronics. As we demonstrate in this work, some hydrides have the potential to solve the above mentioned problems.

Hydrides have intensively been studied so far for their application as hydrogen storage/economy⁷ and smart windows.^{8,9} For these purposes acceleration of kinetics of hydrogenation/dehydrogenation processes, lowering the temperature at which the hydrogenation/dehydrogenation occurs, to increasing the hydrogen content, and lowering the weight of hydrides are extremely important. Furthermore, hydrides in powder form are found to be more appropriate. Recently, it was suggested that hydrides can be considered as novel class of semiconductors¹⁰ and transparent conducting materials.¹¹ To our knowledge, there is no experimental study of crystalline or amorphous hydrides and their potential for application in semiconductor electronics and PV. Also, the question as to whether there are the hydrides, which possess almost the same electrical and optical properties as the commonly used crystalline Si and *a*-Si:H is open. The aim of this paper is to perform comparative analysis of electronic structure and optical properties of Mg₂NiH₄ in cubic (*c*) (bulk and doped) and monoclinic (*m*) modifications with Si and *a*-Si:H. We show that hydrides have the potential to replace Si and *a*-Si:H.

VASP-PAW package^{12, 13} has been used in the present study along with generalized-gradient approximation of Perdew-Wang¹⁴. Lattice relaxation was performed by using the conjugate gradient method. The plane-wave cutoff energy of 500 eV was used for all the calculations. The convergence was achieved when the forces acting on the atoms were smaller than 20 meV Å⁻¹ and the total energy difference between two consecutive iterations were < 10⁻⁶ eV. The convergence criteria and more details about the optical calculations were discussed in Ref. ¹⁵. Effective density of states (DOS) and DOS masses have been calculated from the total DOS (TDOS) derived from DFT calculations. Optical effective masses have been calculated by:

$$\frac{1}{m_c(\mathbf{k})} = \frac{1}{\hbar^2} \left. \frac{\partial^2 E(\mathbf{k})}{\partial \mathbf{k}^2} \right|_{\mathbf{k}=\mathbf{k}_0} \quad (1)$$

in the close vicinity of the band extremum in the energy range 25-300 meV by polynomial fitting.

The imaginary part of the optical dielectric function $\varepsilon_2(\omega)$ has been derived by summing all allowed transitions from occupied to unoccupied states for energies much higher than those of the phonons. It is used to derive the reflectivity $R(\omega)$ and absorption $\alpha(\omega)$ coefficients as well as refractive index $n(\omega)$. More details about the optical calculations were discussed in Refs. ¹⁵.

Structural information for Mg_2NiH_4 -*c* and *-m* were obtained from Refs. ¹⁶⁻¹⁸, while that for Si was obtained from Ref. ¹⁹. Formation energy for Li_{Mg} and Al_{Mg} doped cubic (*c*) Mg_2NiH_4 has been calculated as²⁰

$$E^f(D^q) = E_{\text{tot}}(D^q) - E_{\text{tot}}(\text{Mg}_2\text{NiH}_4) + n_{\text{Mg}}\mu_{\text{Mg}} - n_{\text{Li,Al}}\mu_{\text{Li,Al}} + qE_F. \quad (2)$$

Here $E_{\text{tot}}(D^q)$ the total energy of the lattice with an impurity D in charge state q . $E_{\text{tot}}(\text{Mg}_2\text{NiH}_4)$ is the total energy of the perfect Mg_2NiH_4 crystal in the same supercell. E_F is the Fermi energy. μ_{Mg} and $\mu_{\text{Li,Al}}$ are the chemical potentials of Mg, Li, and Al, respectively.

We have considered Mg_2NiH_4 in cubic (*c*) and monoclinic (*m*) modifications. We have chosen the hydride because it is well studied theoretically and experimentally.^{17, 21-}
²³ Furthermore, n^+ - n junction has been obtained²¹ from the hydride. To demonstrate similarity of band structures and optical properties of hydrides with those of semiconductors and to suggest applicability of hydrides for p - n junction based devices we have performed comparative analysis of band gap and optical properties of Si and

Mg₂NiH₄.

Figure 1 presents band structure of Si and Mg₂NiH_{4-c} and -*m*. It is seen that band structure of *c*-Si is similar to that of Mg₂NiH_{4-c}. Namely, both possess indirect gap with topmost valence band (VB) located at the Γ point and bottommost conduction band (CB) located at the *X* point. The calculated fundamental band gaps (E_g) have been underestimated because of the well known deficiency of DFT and found to be equal to 0.71 eV for Si, 0.17 eV for Mg₂NiH_{4-c}, and 1.65 eV for Mg₂NiH_{4-m}. These results are in close agreement with those of Refs.^{16,17,24}. One of the ways to correct the deficiency is rigid shift of the CBs up to experimentally determined location. This way has been applied and the band gap has been increased up to 1.1 eV for Si, 1.3 eV for Mg₂NiH_{4-c} ($E_g \sim 1.3-1.5$ eV^{16, 17}), and 1.7 eV for Mg₂NiH_{4-m} ($E_g \sim 1.7-1.9$ eV^{16, 17, 24}). It is seen that experimentally determined band gap of Si is close to that of Mg₂NiH_{4-c} whereas the band gap of Mg₂NiH_{4-m} is similar to that of *a*-Si:H ($E_g \sim 1.7-1.9$ eV).⁶

Despite similarity in band structure and band gaps, the origin of the topmost part of VB and bottommost part of CB of the hydrides considered in this work are completely different than those of the Si and *a*-Si:H. Figure 2 displays orbital and site projected density of states. It is seen that topmost VB(CB) of Si is strongly contributed by Si 3*p*(3*s*) electrons, whereas both lowest CB and upmost VB of Mg₂NiH₄ has strong contribution from Ni 3*d* electrons. Hence, optical transition from the topmost VB to the bottommost CB of Mg₂NiH₄ can be forbidden. As a result, the photon energy range for which Mg₂NiH₄ is transparent, can be larger than its fundamental band gap. That can be the reason of transparency of Mg₂NiH₄ to visible part of solar spectra despite its small fundamental band gap <1.9 eV. Similar to that of TCOs, e.g., anatase Ti_{1-x}Nb_xO₂,²⁵ Mg₂NiH₄ can be considered as *d* electron based semiconductor. This is distinguishing

features of some transition metal hydrides. Commonly topmost VB of hydrides have contributed from s electrons.^{10, 11}

Analysis of Fig. 1 shows that the bottommost CB and topmost VB are well dispersive for Si and polymorphs of Mg_2NiH_4 . It shows that the Mg_2NiH_4 phases can be capable for transport of electrical current. For quantitative characterization of the band dispersion, effective masses of holes (m_h) have been calculated (Table I). It is seen that the calculated CB masses for $\text{Mg}_2\text{NiH}_{4-c}$ along $\Gamma \rightarrow X$ is in good agreement with those for Si calculated in the present work and determined experimentally. Order of magnitude of the hole effective masses for $\text{Mg}_2\text{NiH}_{4-c}$ and $-m$ is the same as those for Si. CB effective mass for $\text{Mg}_2\text{NiH}_{4-m}$ has not been calculated since it is almost flat at the band extremum. Not only band structure, but also effective masses for Si and $\text{Mg}_2\text{NiH}_{4-c}$ are close to each other.

Figure 3 displays optical spectra for these compounds. Because of the underestimation of the calculated band gap, the calculated optical spectra commonly are shifted toward lower energies. To fix this error rigid shift of the optical spectra has been applied for Si to higher energies up to the experimentally established value. It is seen in Fig. 3 that general features of the experimentally measured optical properties of Si in the visible spectra of solar radiation have been reproduced in the theoretical calculations, which indicates that the theoretical calculations are reliable. Since there are no such experimental data for optical properties of $\text{Mg}_2\text{NiH}_{4-c}$, and $-m$, rigid shift has not been applied for these Mg_2NiH_4 polymorphs. For this reason, all the optical spectra of the Mg_2NiH_4 polymorphs have been shifted toward lower energies than Si and $a\text{-Si:H}$. The real optical spectra for the hydrides are expected to start at larger energies than those demonstrated in Fig. 3. Analysis of Fig. 3 shows that the magnitude of the

absorption coefficient of $\text{Mg}_2\text{NiH}_{4-c}$ at the fundamental absorption edge is almost the same as that of Si. However, reflectivity $R(\omega)$ and refractive index $n(\omega)$ of $\text{Mg}_2\text{NiH}_{4-c}$ in the visible region of the solar spectra are smaller than those of Si. In case of Si the large values of $R(\omega)$ and $n(\omega)$ is commonly compensated by using antireflective coatings. Consequently, the smaller values of $R(\omega)$ and $n(\omega)$ can be considered as advantage of $\text{Mg}_2\text{NiH}_{4-c}$ over Si. Analysis of Fig. 3 shows that not only absorption spectra $\alpha(\omega)$, but also reflectivity $R(\omega)$ and refractive index $n(\omega)$ of $\text{Mg}_2\text{NiH}_{4-m}$ is also smaller than those of *a*-Si:H.

To design hydride based electronic devices the information as to capability of the hydrides to possess *n*-/*p*-type electrical conductivity is also extremely important. Upon doping Si with higher/lower valence impurity atoms such as, say P/B, the impurities are known to substitute Si site and form shallow donor/acceptor impurities, which can easily be ionized at room temperature and be the source for *n*-/*p*-type electrical conductivity. Based on this knowledge we have studied the question as to whether higher/lower valence impurities substituting, say Mg, can be the shallow donors/acceptors, which could also provide *n*-/*p*-type electrical conductivity. For these purposes we have studied structural properties, electronic structure and optical spectra of Li_{Mg} and Al_{Mg} doped $\text{Mg}_2\text{NiH}_{4-c}$: From structural studies we found that the volume of the Li(Al) doped $\text{Mg}_2\text{NiH}_{4-c}$ has been increased to 0.28% (0.11%) compared to the ideal one. Figure 4 displays total DOS for the Li(Al) doped $\text{Mg}_2\text{NiH}_{4-c}$. It is seen that when Li(Al) substitutes Mg, it forms a shallow level acceptor(donor). However, the formation energy for the Li(Al) doped $\text{Mg}_2\text{NiH}_{4-c}$ calculated by the Eq. (2) is -0.90(+1.19) eV, which shows that Li_{Mg} is stable, but Al_{Mg} is less stable. It should be

noted that for design of semiconductor p - n junction, heavy doping is not required as in the case of transparent conducting materials.^{26, 27}

Fig. 5 shows optical spectra for $\text{Mg}_2\text{NiH}_4\text{-}c\text{:Li}_{\text{Mg}}(\text{Al}_{\text{Mg}})$. As it is seen heavy doping with shallow level impurities drastically changes optical properties of $\text{Mg}_2\text{NiH}_4\text{-}c$. Optical transition between the shallow level band and VB/CB causes huge increase of absorption and reflectivity. The shallow level impurities can increase not only absorption spectra, but also reflectivity. However, when the doping level is small $<10^{15}$ cm^{-3} , huge increase of reflectivity because of the doping is not expected.

It should be noted that hydrides can be used as buffer layer in between semiconductor and TCO. Previously, in Si based heterojunction solar cells $a\text{-Si:H}$ with band gap 1.7-1.9 eV has been used.²⁸⁻³⁰ Band gap of $\text{Mg}_2\text{NiH}_4\text{-}m$ is almost the same as that of $a\text{-Si:H}$. It indicates that hydrides can replace $a\text{-Si:H}$. As noted above, distinct from $a\text{-Si:H}$, $\text{Mg}_2\text{NiH}_4\text{-}m$ is crystalline and one can expect from crystalline solids better electrical properties than amorphous materials. Doping of $\text{Mg}_2\text{NiH}_4\text{-}m$ with shallow level impurities is the subject of future studies.

In conclusion, we have demonstrated by DFT calculations that electronic structure, some transport parameters, and optical properties of cubic Mg_2NiH_4 is similar to that of crystalline Si, whereas those of monoclinic Mg_2NiH_4 is similar to those of $a\text{-Si:H}$. Reflectivity and refractive index of the hydrides are found to be smaller than those of Si and $a\text{-Si:H}$. Based on these analysis hydrides are concluded to have the potential to replace conventional semiconductors and be used in semiconductor electronics, e.g., as solar cell materials.

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Table I. Fundamental band gap (E_g) (in eV) calculated by DFT and determined experimentally, effective DOS (cm^{-3}) for electrons (N_c) and holes (N_v), intrinsic carrier concentration (n_i , cm^{-3}), density of states mass for electrons (m_{de}) and holes (m_{dh}), CB (m_c) and VB (m_h) electron effective masses (in units of the free electron mass m_0) for Mg_2NiH_4 -*c*, -*m*, Si, and a-Si:H. Experimentally determined band gap has been used in estimation of the intrinsic carrier concentrations.

Compound	E_g	N_c , ($\times 10^{19}$)	N_v , ($\times 10^{19}$)	n_i , ($\times 10^9$)	m_{de}	m_{dh}	m_c	m_h
Mg_2NiH_4 - <i>c</i>	1.3	0.58	0.11	0.03	0.38	0.12	1.02($\Gamma \rightarrow X$) 0.19($X \rightarrow K$)	0.84($\Gamma \rightarrow X$) 0.71($\Gamma \rightarrow L$)
Mg_2NiH_4 - <i>m</i>	1.65	0.02	1.37	0.0002	0.04	0.67		1.12($\Gamma \rightarrow A$) 0.93($\Gamma \rightarrow Z$)
Si, Theory	0.70	0.40	0.06	0.62	0.29	0.08	1.09	0.27 ($\Gamma \rightarrow X$), 0.79 ($\Gamma \rightarrow L$)
Si, Exp	1.12 ^a	2.90 ^a	3.10 ^a	12.00 ^a	1.10 ^a	1.15 ^a	1.08 ^b	0.217 ^c ($\Gamma \rightarrow X$) 0.541 ^d ($\Gamma \rightarrow L$)

^aExperiment.³¹

^b) Experiment.³²

^c) Experiment.³³

^d) k.p theory, semiempirical results.³⁴

Figure captions

Fig. 1. Band dispersion for Si, Mg₂NiH_{4-c}, and Mg₂NiH_{4-m}. Fermi level is set at zero energy.

Fig. 2. Orbital and site projected DOS for Si and Mg₂NiH_{4-c}. Fermi level is set at zero energy.

Fig. 3. Calculated imaginary part of the optical dielectric function $\varepsilon_2(\omega)$, absorption coefficient $\alpha(\omega)$ (in cm⁻¹ divided by 10⁵), reflectivity $R(\omega)$, and extinction coefficient $n(\omega)$ for Si, Mg₂NiH_{4-c} and Mg₂NiH_{4-m} along with experimentally measured ones for crystalline Si and a-Si:H.³⁵

Fig. 4. Total DOS for Mg₂NiH_{4-c} doped with Al_{Mg} and Li_{Mg} along with that for bulk Mg₂NiH_{4-c}.

Fig. 5. Calculated imaginary part of the optical dielectric function $\varepsilon_2(\omega)$, absorption coefficient $\alpha(\omega)$ (in cm⁻¹ divided by 10⁵), reflectivity $R(\omega)$, and extinction coefficient $n(\omega)$ for Mg₂NiH_{4-c} doped with Li_{Mg} and Al_{Mg} as compared to those for undoped Mg₂NiH_{4-c}.