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连续激光诱导 Ni 掺杂过饱和单晶 Si 材料的探索

Exploration of Supersaturated Ni-doped Monocrystalline Silicon Material Prepared by Continuous-wave Laser Irradiation

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摘 要

由于过饱和掺杂的硅基杂质中间带材料在中间带太阳电池和红外探测器等领域具有良好的应用前景，近年来受到了各国科研工作者的广泛关注和研究。本文首次选用Ni作为掺杂元素，从理论和实验两方面对Ni掺杂过饱和单晶Si材料形成中间带的可行性进行了探索。理论方面，基于密度泛函理论(DFT)对Ni掺杂体Si的形成能、电子结构和光学性质进行了第一性原理计算。实验方面，采用溅射镀膜结合连续线形激光扫描的方法成功制备了Ni掺杂过饱和单晶Si材料；并对Ni掺杂过饱和单晶Si材料的结晶特性与光电特性进行了表征与分析。本文所开展的研究工作及主要研究结果如下:

1. 基于第一性原理计算研究了 Ni 间隙和替位掺杂体 Si 后的结构稳定性、电子结构与光学性质。结论如下:(1) Ni 以间隙位的形式存在于 Si 的晶格中最稳定。(2) 间隙位 Ni 掺杂体 Si 后在导带底(CBM)下方几十电子毫伏的位置出现了一个独立的、空的能带。这个能带在能量上与导带底有很大的交叠，故也可看做导带底。将这个能带看做导带底后，材料为直接带隙半导体，禁带变窄，禁带宽度约为体硅的 0.85 倍，价带顶（VBM）的态密度有显著增大。(3)替代位 Ni 掺杂体 Si 后在 Si 的禁带中引入一个独立的、半满中间带(IB)。这个中间带主要来自 Ni-d 和 Si-p 态电子的贡献，位于导带下方几百电子毫伏的位置。掺杂后的材料禁带变宽，禁带宽度约为体 Si 的 1.2 倍，VBM 和 CBM 对应的高对称点位置都有所变化。由于形成了半满中间带，Ni 替代掺杂体 Si 后所得材料在低温时的电导率将具有“类金属性”；在近红外波段内的子带光吸收都有显著增加。(4)虽然间隙 Ni 掺杂 Si 无法单独形成杂质中间带；但当其与替代位 Ni 共同掺杂 Si 时，杂质中间带有贡献。

2. 采用磁控溅射和连续线形激光（Nd:YAG）诱导掺杂的方法制备得到了 Ni 掺杂过饱和单晶 Si 材料。优化得到了一组制备样品的最佳工艺参数为:(1)Ni 薄膜的厚度设置为 80 nm；(2)加热台的温度设置为 250℃；(3)连续线形激光器的输出功率设置为 200 W；(4)二维加热台移动的速度设置为 2 mm/s；(5)激光扫描

次数为 6 次。在此工艺参数条件下制备得到的 Ni 掺杂过饱和单晶 Si 材料的过饱和层，在距离表面 35 nm 区域厚度内，Ni 原子的浓度超过了 Mott 浓度 5.9×10^{19} cm^{-3}。

3. 对 Ni 掺杂过饱和单晶 Si 材料的结晶特性进行了表征，并研究了激光扫描次数对样品结晶性的影响。激光扫描次数小于 6 次时对结晶性影响很小；大于 6 次后在 p-Si:Ni 样品中在距离表面几十纳米区域内开始形成团簇颗粒，当扫描次数达到 11 次时团簇颗粒的直径尺寸达到几个纳米数量级；Ni 过饱和掺杂层主要包含 Ni、O、Si 三种元素。激光扫描次数为 16 次时，样品结晶特性明显变差。

4. 对 Ni 掺杂过饱和单晶 Si 表面 Ni 掺杂层的载流子浓度进行了表征，并研究了激光扫描次数对表面 Ni 掺杂层载流子浓度的影响。激光扫描镀有 Ni 薄膜的晶 Si 样品会使 p-Si:Ni 样品表面区域的载流子浓度发生显著改变；随着激光扫描次数的不同载流子的导电类型和浓度也有不同。随着激光扫描次数的增加，表面掺杂层的载流子类型及浓度依次经历了从 p→p+→n+→p+的变化过程。

5. 对 Ni 掺杂过饱和单晶 Si 材料的电学特性进行了表征。在 80~300 K 温度区间内 p-Si:Ni 样品的载流子浓度出现了一个极值，预示着 p-Si:Ni 样品中可能至少有两个能带参与导电，这两个能带中可能包含了杂质带。采用双能带导电模型对载流子浓度的温度相关性进行拟合与分析。同时，室温(300K)少子寿命测试表明 p-Si:Ni 样品的平均少子寿命约为 42 μs，较未掺杂的 p-Si 衬底(平均少子寿命约 5 μs)有显著提高。

6. 对 Ni 掺杂过饱和单晶 Si 材料在室温下的光学特性和光电响应进行了表征。光学测试结果表明，在波长大于 1200 nm 光波的光照下，p-Si:Ni 样品近红外光的吸收显著增强；表面光伏谱（SPVS）测试与外量子效率（EQE）测试也均出现了明显的光电响应，这些结果同时说明在 p-Si:Ni 材料的能带结构中可能形成了杂质中间带。

关键词： 连续激光诱导；中间带； Ni 掺杂；过饱和单晶 Si；第一性原理

Abstract

In recent years, the supersaturated Si-based materials have been widely investigated due to its good application prospects in the fields of solar cells and infrared detectors. In this thesis, the formation feasibility of a Si-based intermediate band (IB) material through continuous-wave laser induced supersaturated Ni-doping has been explored for the first time in both theoretical and experimental aspects. First-principles calculations based on the density-functional theory have been carried out to study the formation energy, the electronic structure, and the optical property of the Ni-doped bulk Si with different structures. The Ni supersaturated Si samples have been successfully prepared using a simple method, which combined magnetron sputtering with continuous-wave laser scanning. The crystalinity and the optoelectronic properties have been characterized and analyzed to verify the formation of a Ni-related intermediate band. The main conclusions of this work are summarized as follows:

1. The results of first-principles calculations indicate that: (1) Interstitial Ni is more stable than substitutional Ni when Ni existed in bulk Si as a single dopant atom. (2) Interstitial Ni doping in bulk Si introduced a separate and empty band at about dozens of meV below the conduction band. This empty band mainly consisted of Si-2p orbital electrons, and overlapped with conduction band in the energy distribution, so this band can be considered as the conduction band minimum (CBM). In this case, the interstitial Ni doped Si became a direct-band semiconductor with a smaller bandgap，which is about 0.85 times as large as that of bulk Si, and the density of states around the valance band maximum (VBM) increased a lot. (3) Substitutional Ni doping in bulk Si introduced a separate and half-full IB, which was mainly contributed by Ni-3d and Si-2p orbital electrons and located at about several tenths of eV below the conduction band. The bandgap between CBM and VBM is about 1.2

times as large as that of Si, and the locations of high symmetry points corresponding to the VBM and CBM have been changed. Due to the half-full of IB, the substitutional Ni doped Si would exhibit a “metal-like” electronic property in the low temperature and strong sub-band absorption optical property in the near-infrared light area. (4) Although interstitial Ni doping in bulk Si cannot independently introduce a separate and half-full IB, when it co-dopes with substitutional Ni in bulk Si, it would contribute to the IB.

2. The Ni supersaturated p-type Si samples have been prepared successfully using a method of magnetron sputtering and continuous-wave laser scanning. Moreover, a group of optimized process parameters was obtained as follows: (1) The depth of the Ni film was 80 nm; (2) The temperature of the heating unit was 250℃；(3) The output power of the laser was 200 W；(4) The velocity of the heating unit was 2 mm/s；(5) The times of Laser scanning were 6. Using this group of process parameters, the Ni concentration in the surface layer exceeded the Mott limit of 5.9×10^{19} cm^{-3} within a thickness of about 35 nm.

3. The crystalinity of the Ni supersaturated Si has been characterized and its dependence on the times of laser scanning has been discussed as well. When laser scanning times were less than 6, it affected little on the lattice structure. When scanning times were more than 6, some particle clusters started to form in the Ni-doped layer, and then grew up with the increase of scanning times. The Ni-doped layer mainly consisted of Si, Ni and O. When scanning times were more than 16, the lattice structure would change a lot.

4. The carrier concentration of the Ni doped layer has been characterized and its dependence on the laser scanning times has been discussed as well. Laser scanning process could significantly change the carrier concentration of the surface layer of the Ni-doped Si, and the conduction type and the concentration of the carrier were dependent on the laser scanning times. As the laser scanning times increased from 1 to 16, the conduction type and the concentration of the carrier experienced a change of

p→p+→n+→p+.

5. The electronic properties of the Ni supersaturated Si have been characterized. Between 80 and 300 K, the carrier concentration of the Ni supersaturated Si showed an extreme value, which indicated that there may exist an impurity IB contributing to the measured carrier concentration in addition to the conduction band. A two-band model has been used to interpret the temperature-dependent carrier concentration. Moreover, the location and the concentration of the impurity level were obtained through numerical fitting. A measurement of lifetime was carried out at RT, which showed that the average lifetime of the Ni supersaturated Si sample was about 42 μs. The average lifetime of the Ni supersaturated Si increased significantly compared to the undoped p-Si substrate (the average lifetime was about 5 μs).

6. The room-temperature (RT) optical and optoelectronic properties of the Ni supersaturated Si have been characterized. Beyond 1200 nm, the Ni supersaturated Si exhibited a significant increase of the optical absorption. Furthermore, both the surface photovoltaic spectra (SPVS) and external quantum efficiency (EQE) measurements presented apparent subband gap optoelectronic response, which substantiated the formation of an IB in the energy band of the Ni supersaturated Si sample.

Keywords: Continuous-wave laser scanning; Intermediate band; Ni doping; Supersaturated Si; First-principles caculations

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