A Stable Porous Silicon Dielectric Reflector with a Photonic Band Gap Centred at 10 µm

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By pulsed anodic etching at low temperature, we prepared a porous silicon reflector with a photonic band gap centred in the long-wavelength infrared spectral region (centred at about 12 µm). After proper oxidation process, the stable reflector structure, which can reflect electromagnetic wave from 8 µm to 12 µm (centred at 10 µm) within wide incidence angles (about 50°), is obtained. The wavelength shift of absorption peak of Si–H and Si–O shows the influence of oxidation process and indicates the stability of oxidized porous silicon dielectric reflector, which offers possible applications for the room temperature infrared sensor.

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The long-wavelength infrared (LWIR) region 8–14 µm (centred at 10 µm) is an especial electromagnetic (EM) wave range which has attracted much attention because it is an atmospheric transmission window and many daily objects, including animals and people, are radiation objects with infrared (IR) radiation in this wavelength region. Since many objects emit apparent IR radiation, the related IR devices work on this LWIR spectral region has drawn much attention. Meanwhile, the IR devices have a wide variety of applications in scientific measurements, including industrial computers, wireless transmission, environmental protection, military equipment and etc. Among these devices, the dielectric reflector has been extensively studied because of its easy preparation and wide use. The chemical vapour deposition (CVD) is used to form Si/SiO₂ double structure to reflect EM wave in both thermal atmospheric windows 3–5 µm and 8–13 µm and to suppress the thermal emission. Based on the photonic crystal theory, the vacuum evaporated method is used to form the dielectric omnidirectional reflector in reflectance region 9–15 µm.

Porous silicon (PSi) is considered as a promising material for photonic application due to its low cost and good compatibility with silicon manufacture. In the process of PSi formation in solution containing hydrofluoric acid (HF) by electrochemical etching, the porosity of a PSi layer can be controlled by adjusting the etching conditions, such as current density, anodization time, HF concentration and etc. In this case, PSi distributed Bragg reflectors (DBR) are made by periodically stacking a number of PSi layers of alternating high and low refractive materials, which means alternating layers of low and high porosity layers in the case of PSi. The reflectance regions of the PSi reflector are mainly in two wavelength regions, one is visible and near-infrared region (from 400–1000 nm) in order to form the PSi DBR and Fabry–Perot microcavity as well as to control the light emission from PSi. The other one is about 1500 nm region for applications in the optical communication device. PSi reflector work on the LWIR region (about 10 µm) has not been reported. As we know, thickness of the PSi layer will grow thicker (about several tens of micrometres) and will turn into high porosity (> 70%) as the photonic band gap (PBG) shift to LWIR while the refractive index of PSi layer almost does not change dramatically. In this case, during anodic etching process, bubbles on the wall surfaces of the pores and the reduction of HF concentration inside the pores, which is the result of the chemical reduction of HF with silicon, may slow down the etching process and the PBG shift to LWIR. Meanwhile, PSi layer structures are mechanically unstable and may cause crack during drying process due to the effect of capillary pressure within the pores.

In order to obtain PSi thin films with larger thickness and porosity, different methods are adopted in the anodic etching process. One method is the pulsed anodic etching. Hou et al. have indicated the porous silicon layer prepared by pulsed anodic etching method has a more uniform film structure with the larger thickness and steeper sidewalls compared with the de etched PSi sample. By means of choosing the suitable ratio of etching time and break time, the PSi...
dielectric reflector with the PBG centred at 2.5 µm has been obtained.\[12\] The second method is low temperature solution. In this case, strong decrease of the roughness and increase of the porosity can be obtained at low temperature anodization. At low temperatures, a decrease in the ion mobility causes a higher rate of electro-polishing, which tends to smooth out the inhomogeneities at the interfaces resulting in less scattering and hence better quality devices.\[13\] Thus, the refractive index difference between adjacent layers of the multilayered structure is maximized for low temperature fabrication process. The PSI dielectric reflector with PBG centred at 3.0 µm was obtained at the low temperature of −27°C.\[14\]

In the present work, in order to obtain a stable porous silicon dielectric reflector with a photonic band gap (PBG) centred at 10 µm, first, a porous silicon reflector with a PBG centred at 12 µm wavelength region is prepared by pulsed anodic etching at low temperature, and after proper oxidation process, we obtain the stable PSI reflector structure which can reflect EM wave from 8 µm to 12 µm (centred at 10 µm).

In this Letter, silicon wafer, boron-doped (0.01Ωcm) (100) oriented, is employed for the preparation of 1D photonic crystal. HF (40%), mixed with ethanol by 1:1 (V/V), serves as electrolyte. Electrochemical etching is applied to fabricate porous silicon multilayer. The multilayer is fabricated by pulsed anodic etching with the current density of 10 and 70 mA/cm² with the repetition rates of 1 Hz, duty cycles of 1:1, controlled by a computer with a high reproducibility. The etching cell is kept at −27°C. In order to obtain a stable PSI reflector in the atmosphere, the prepared multiplayer PSI structure is oxidized at 500°C for 20 min by rapid thermal oxidation (RTO), in an ambient of 1.013 kPa with a constant oxygen flux (0.6 L/min). Fourier transform infrared spectroscopy (FTIR, Thermo Company, NICOLET 5700) is conducted at room temperature to measure its optical reflectance. The reflective spectra were normalized by a silver film.

As PSI is exposed to the air, PBG of PSI reflector will shift to the short wavelength during the oxidation process due to the decrease of the refractive index of the PSI layer. In this case, in order to obtain the stable PSI reflector centred at 10 µm, PBG of the PSI reflector must be larger than 10 µm. As shown in Fig. 1(a), a PSI dielectric reflector with a regime of high reflectance from about 10 µm to 14 µm, and the central wavelength about 12 µm is prepared by pulsed anodic etching at low temperature (−27°C). As the spectral shows, a little dip exists at 11.04 µm (906 cm⁻¹) in the high reflectance region. The LWIR enters the spectral region of the molecular vibration and the dip is attributed to an absorption band, associated with the stretching and deformation of Si–H₂, which confines that PSI reflectors are passivated by hydrogen and lack of oxygen.\[15,16\] However, when the fresh PSI sample is exposed to air, the Si–O feature will still appear and gradually become dominant. Meanwhile, PBG of PSI reflector will shift to the short wavelength because of the lower refractive index of SiO₂ compared with that of Si. In order to obtain the stable PSI reflector, the prepared multiplayer PSI structure is oxidized at 500°C for 20 min. It is found\[14\] that oxidation of the multiplayer structure at these parameters will result in full oxidation of the layer with high porosity and partial oxidation of the layer with low porosity, which means that there will be a contrast of the refractive indices between the layers with low as well as high porosities. The reflectance spectrum of the oxidized PSI reflector is shown in the Fig. 1(b). It is found that the PBG, centred at 10 µm with the high reflectance regimes from about 8 µm to 12 µm, has been obtained. At the same time, a dip at about 7.989 µm (about 1250 cm⁻¹) can be found, associated with the absorption band of Si-Oₓ. Meanwhile the absorption band of the Si-H at 11 µm disappears. The oxidation process replacing Si-H₂ bonds by Si-O₂ has indicated the total surface chemical coverage of oxide at the PSI surface. In this case, we believe that the stable reflector structure reflecting EM wave from 8 µm to 12 µm (centred at 10 µm) can be obtained.

![Fig. 1. Experimental (line) and theoretical (dots) reflectance spectra of the porous silicon reflector before (a) and after (b) oxidation.](image-url)
highly consistent with the experimental spectra. The simulations also determine the optical parameters of PSi reflectance, which indicates that layer etched by high current density has a refractive index of 1.35 and layer etched by low current density 2.34. After oxidation at 500°C for 20 min, the refractive index of high porosity layer slightly drops to 1.25; the refractive index of the low porosity layer goes down to 1.84. In this case, the width of the band gap is reduced because of the decrease of the ratio in the indices, but the almost fully oxidization of high porosity layer will make the PSI reflector stable.

![Fig. 2. Experimental reflectance spectra of the porous silicon reflector before oxidation for incidence angle 10° (a), 15° (b), 30° (c), and 50° (d).](image)

As a dielectric reflector, it is essential to ensure that it can reflect EM wave within wide incidence angles and FTIR is applied to discuss this feature. Figures 2 and 3 show the reflectance spectra versus incidence angles of the anodized sample before and after oxidation. A, B, C, and D in both the figures stand for the incidence angles of 10°, 15°, 30°, and 50°, respectively. Figure 2 shows that PBG of reflector shifts to the short wavelength as the incidence angle increases. However, even at the incidence angle (50°), PBG band still fits the centred wavelength 12 µm (before oxidation) and 10 µm (after oxidation), respectively. It must be pointed out that our PSI reflector is not the omnidirectional reflector due to its lower ration of refractive indices (only 1.84/1.25) but it is possible to obtain the internal omnidirectional reflector with the simple parameters altering and adding the stacked layer on the top of reflector.

A dip at about 11.03 µm (906 cm⁻¹), which does not shift with the incidence angles must be noticed. This gives another point that the dip is not the structure oscillation peak but the absorption band of material, and we insist our former discussion that it is the absorption band of Si-H₂. Meanwhile, as shown in Fig. 3, a dip at about 7.897 µm means the absorbance peak of Si-Oₓ.

As the number of periods of the multilayer increases, the reflectance of the dielectric reflector will be improved. However, such an increment of the periodic number is limited by the stability of the PSi sample. Collapse occurs when the periodic number reaches 12. Our experimental data indicate that even this multilayer structure is only 5 pairs of PSi layers; the high reflectance region can be suitable to device application.

![Fig. 3. Experimental reflectance spectra of the porous silicon reflector after oxidation for incidence angle 10° (a), 15° (b), 30° (c), and 50° (d).](image)

In summary, after proper oxidation, a stable reflector based on porous silicon has been prepared within PBG centred at 10 µm, the wavelength of the atmo-
sphere at room temperature. Its optical feature proves to be stable and this kind of substrate is promising in sensor application.

References