TWO-DIMENSIONAL EXCITONS IN SILOXENE

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ABSTRACT

The luminescence properties of two different modifications of siloxene are studied with photoluminescence excitation spectroscopy (PLE) und optically detected magnetic resonance (ODMR). The luminescence of as prepared siloxene, which consists of isolated silicon planes, is resonantly excited at the bandgap, indicating a direct bandstructure. The observation of $\Delta m = \pm 2$ transitions in ODMR shows that triplet excitons contribute to the luminescence process. In contrast, annealed siloxene consisting primarily of six-membered silicon rings shows a PLE typical of a material with an indirect bandgap. The ODMR signal of annealed siloxene and of porous silicon show the same Gaussian line with a typical width of 400 G, which can arise from strong dipolar coupling of an electron and a hole $\approx 5\text{\AA}$ apart.

INTRODUCTION

To integrate optoelectronic devices with silicon microelectronics, it would be highly desirable to use silicon-based materials also for light-emitting structures. Due to its bandstructure with an indirect bandgap of about 1.1 eV, crystalline silicon does not show visible light emission at room temperature, so that the bandstructure restrictions have to be relaxed considerably to obtain efficient luminescence. This can either be achieved by structural disorder in wide-bandgap amorphous silicon alloys such as $a-SiH_x$, $a-SiC_x$, $a-SiO_x$ or $a-SiN_x$, or possibly by quantum confinement in crystallites or undulating wires of typically 10-20Å diameter, which has been proposed as the cause for the red photoluminescence from anodically oxidized porous silicon. A third way is to reduce the dimensionality of the silicon backbone from 3 in the case of crystalline or amorphous material to 2 as in planar polysilane $(SiH)_n$ and in siloxene $(Si_6O_3H_6)_n$ or to 1 as in linear polysilanes $(SiH_2)_n$. While amorphous silicon and its alloys as well as polysilane have been studied quite extensively, and while porous silicon has received considerable attention in the last two years, the planar silicon modifications have been basically overlooked. Our recent observation of virtually identical luminescence properties of porous silicon and of a specific modification of siloxene, which is characterized mainly by rings made of six silicon atoms which are isolated from adjacent rings by oxygen bridges, has renewed the interest in this kind of material. In the following, we will study some fundamental photoluminescence properties of siloxene using photoluminescence excitation spectroscopy and optically detected magnetic resonance.

PREPARATION OF LUMINECENT TWO-DIMENSIONAL SILICON BACKBONES

To date, the only known way to produce two-dimensional silicon backbones is by starting from $CaSi_2$ [1]. This silicide itself has a two-dimensional structure consisting of the silicon (111) double layers as found in crystalline silicon, which are in this substance seperated from each other by layers of calcium. Inserting $CaSi_2$ in HCl leads to the removal of Ca by the formation of $CaCl_2$, the dangling bonds generated by this procedure are saturated by H- or OH-groups (Fig. 1). The exact percentage of saturation by the respective groups and therefore the stochiometry of the final material depends strongly on the preparation conditions. Numerous attempts have been reported to produce pure planar polysilane (SiH)_n by excluding any oxygen from the wet chemical process sketched above [2,3]. The substances obtained are highly reactive and have therefore not been





subject to thorough investigation. In contrast, stable materials are usually obtained when water is present during the reaction. One typically finds a stochiometry of $(Si_6O_3H_6)_n$ and the material is called siloxene [4]. The crystallographic structure has been repeatedly established with the help of X-ray diffraction measurements [5,6]. The lattice constant in the Si-layers is decreased by 0.5% with respect to the lattice constant in crystalline silicon, the distance between the layers depends on the preparation conditions but is typically between 5.9 and 7.8Å. The layered structure has recently be confirmed by scanning tunneling microscopy, showing an interlayer spacing of 6Å [7]. The wavelength of the luminescence of siloxene can be shifted by either chemical reactions or brief anneals at 400°C. Infrared spectroscopy shows that the change in the luminescence properties is accompanied by the introduction of oxygen into the silicon planes [8]. If this introduction proceeds in an ordered fashion, rings of six silicon atoms will be formed which are isolated from each other by oxygen bridges. This is the structure of siloxene originally proposed by Kautsky mainly based on arguments concerning the substitution chemistry of the material [4].

OPTICAL PROPERTIES

The specific optical properties of the two modifications of siloxene studied here, the as prepared material and the annealed counterpart, become obvious in the compilation of the photoluminescence (PL) and photoluminescence excitation spectra (PLE) in Fig. 2(b). As prepared siloxene shows a luminescence maximum at around 2.4 eV, while the luminescence of the annealed material peaks at about 1.8 eV. The right hand part of the figure shows the corresponding PLE spectra. While the luminescence of the annealed material is best excited at energies above 3 eV, the luminescence of the as prepared material is excited at 2.6 eV, with very little difference between the excitation and the luminescence maxima.

To understand these different behaviours, we have estimated the optical bandgap of the materials from diffuse reflection measurements, assuming that the absorption is approximately given by 1 minus the reflection. From Fig. 2(a) we obtain a gap energy of ≈ 2.6 eV for as prepared and ≈ 2 eV for annealed siloxene. When comparing the absorption and the excitation spectra it becomes clear that in the as prepared siloxene containing the silicon planes the luminescence is excited resonantly at the bandgap energy. The obvious explanation is that we observe an excitonic transition as expected at the bandgap energy of a direct semiconductor. This interpretation is corroborated by bandstructure calculations, which predict a direct bandgap of 2.7 eV at the Γ point in the planar siloxene modification [9].

Comparison of the absorption and the excitation spectra for annealed siloxene shows that the luminescence of this material is no longer excited at the band edge, but at considerably higher energies of 3-4 eV. Also, the sharp absorption edge has been replaced by a broad tail, which is exponential over nearly two orders of magnitude with a characteristic slope of 200 meV. X-ray



Figure 2: Comparison of the absorption edge as determined from measurements of the diffuse reflectivity (a) and of the photoluminescence excitation (PLE) (b) for as prepared and annealed siloxene.

diffraction shows that the annealed samples consist primarily of an amorphous silicon-oxygen alloy. Calculations for the isolated six-ring structure as the assumed luminescence "center" have indeed shown that the smallest direct transition should be 3-4 eV, with a considerably smaller indirect bandgap. The exact energy of the indirect transition depends on the substitution of the fourth silicon valence, variing from 3 eV for purely hydrogenated rings to 1.9 eV for rings with three hydrogen and three OH-ligands to 1.6 for silicon six-rings completely saturated by OH-groups. The shift of the luminescence to longer wavelengths is therefore accompanied by a significant change in the silicon backbone structure and a change in the type of the lowest transition from direct to indirect.

MICROSCOPIC SIGNATURES OF THE RADIATIVE TRANSITIONS

Further information on the radiative transition can be obtained with the help of optically detected magnetic resonance (ODMR). In this technique, changes in the photoluminescence are detected which occur under electron spin resonance conditions. The basic principle underlying this technique is angular momentum conservation. Only angular momentum conserving transitions are allowed, eg. from certain substates (m = 1, 0, -1) of triplet excitons (S = 1) to the singlet ground state (S = 0). Inducing transitions between the Zeeman-substates will result in a transformation of states not allowed to undergo the radiative transition to states who are allowed to, increasing the overall transition rate of the radiative process and leading to a net enhancement of the luminescence under resonance conditions. The above argument holds for excitons in which both carriers are localized and the orbital angular momentum L is therefore quenched, ie. L = 0. In the case of delocalized carriers, the presence of both L and S allows for more complex transitions which would also satisfy angular momentum conservation.

If a paramagnetic defect is involved as a nonradiative recombination center competing with the radiative recombination, one observes due to the same arguments as presented above an increase in the transition rate at the resonance of the defect. Since a process shunting the radiative transition is now made more probable, the net effect is a quenching of the luminescence. Such a resonant quenching at 100 K is shown for as prepared siloxene in Fig. 3. The conventional electron spin resonance spectrum shows a defect resonance at g=2.0036, typical of silicon dangling bonds, where one of the nearest neighbours of the silicon atoms is oxygen [10]. In agreement with the prediction given above, the 2.4 eV luminescence decreases resonantly.

More relevant to our topic is the resonant enhancement of the luminescence observable at



Figure 3: Electron spin resonance (ESR) and optically detected magnetic resonance (ODMR) of as prepared siloxene. At 100 K only the quenching resonance due to non-radiative recombination through defects is detectable.

lower temperatures. This is shown in Fig. 4 for the two modifications of siloxene studied here. Note that the magnetic field axis extends from 1000 to 5000 G. Both spectra contain three basic spectroscopic features: The narrow quenching line at about $g \approx 2.005$ due to nonradiative recombination through defects as mentioned above, a broad enhancing line around g = 2, which is the microscopic signature of the radiative transition and a feature at half the magnetic field compared to the center of the enhancing resonance, marked as q = 4. Temperature dependent measurements show a rapid decrease in the ODMR signal $\Delta I/I$ with increasing temperature for both the broad enhancing lines at g = 2 and the half-field resonances, while $\Delta I/I$ remains fairly constant for the defect related quenching signal at $g \approx 2.005$. This fact shows that the two first signals have the same origin, namely a triplet exciton where the g = 2 signal corresponds to the spin-allowed $\Delta m = \pm 1$ transitions within the Zeeman-triplet and the g = 4 signal to the forbidden $\Delta m = \pm 2$ transitions. The observation of the half-field resonance for as prepared siloxene corroborates beyond doubt the conclusion already drawn from PLE that exitonic states are responsible for the luminescence, since a $\Delta m = \pm 2$ transition cannot occur in weakly coupled electron-hole pairs. The fact that the ODMR of annealed siloxene also exhibits $\Delta m = \pm 2$ transitions shows that triplet excitons are involved in the indirect transitions in this material as well.

ODMR of the luminescence from low-dimensional systems has been studied only for type II-superlattices, both in the GaAs/AlAs and in the Si/SiGe system [11,12]. Generally, due to the spatial separation of the electrons and holes in adjacent layers of the superlattice separate resonances for the two kinds of carriers are observed. In contrast, the structures of siloxene as determined by X-ray diffraction and the bandstructure calculations discussed above suggest that the carriers will be confined to the same silicon plane or six-ring in this material. In addition, it is known from other materials such as polysilane and oxides, that excitons can be self-trapped due to strong electron-phonon-coupling. Indeed, we observe a strong interaction of the electrons and holes which destroys the separate resonances and leads to the broad resonances of Fig. 4. These enhancing lines are typical for luminescence from amorphous hydrogenated silicon and its wide-bandgap alloys. For a-Si:H, an enhancing line with a typical width of 200 G is found in ODMR [13], with variing reports on the exact lineshape. Alloying with either N or C leads to a gradual increase of the bandgap, which is accompanied by an increase of the luminescence peak energy. At the same time, the linewidth of the enhancing ODMR line increases gradually



Figure 4: Optically detected magnetic resonance of as prepared and annealed siloxene. λ_{lum} : position of luminescence maximum, λ_{det} : detected wavelengths, λ_{ex} : excitation wavelength. The dashed lines show fits of a Lorentzian and a Gaussian to the allowed transitions at g = 2, respectively.

to about 450 G and the line becomes Gaussian [13,14]. The half-field resonances at g = 4 are observed as narrow lines as in annealed siloxene (Fig. 4) [13]. The ODMR of annealed siloxene therefore shows a striking similarity to that of wide-bandgap amorphous silicon alloys.

The interpretation of broad featureless resonances is difficult. Some valuable information can be derived from the actual lineshape. The relevant interaction of the electron and the hole forming the exciton can either be the exchange or the dipolar interaction. The exchange interaction, which in the case of s-wavefunctions with Bohr-radius r_0 and distance r is given by $J = J_0 \exp(-2r/r_0)$, leads to a Lorentzian lineshape [15]. Dipolar broadening, in constrast, leads to a Gaussian lineshape. In this case, the typical distance r of the interacting carriers can be estimated from the width ΔB of the observed resonance line, $r = (\mu_0 g \mu_B / 8\pi \Delta B)^{1/3}$. The experimentally determined linewidth of 400 G for the Gaussian line observed in the ODMR of annealed siloxene then yields a typical distance of about 4.2Å. This is in good agreement with the size of an silicon sixring, which has a diameter of 4.5Å, and thereby corroborates that the luminescence of annealed siloxene originates from states which are localised on the length scale of a six-membered ring. The interpretation of the Lorentzian line and the corresponding step-like half-field resonance will be subject to a forthcoming publication.

As a final note, we would like to state that the ODMR of porous silicon exhibits very similar resonances to that of annealed siloxene, namely an enhancing line at g = 2 with a Gaussian lineshape and the half-field resonance [16]. The linewidth of the g = 2 resonance varies from sample to sample, the typical value is 500 G.

CONCLUSIONS

We have presented ODMR and PLE studies which allow to address in detail the luminescence properties of the different modifications of siloxene. In as prepared material with a planar silicon backbone, the green luminescence at 2.4 eV can best be excited resonantly at the bandgap of 2.6 eV typical for a material with a direct bandgap. After thermal anneal, the luminescence of 1.8 eV is exited nonresonantly above 3 eV. The observation of $\Delta m = \pm 2$ transitions in optically detected magnetic resonance shows that the luminescence from both modifications is indeed due to strongly bound excitonic states. Porous silicon exhibits the same ODMR resonances as annealed siloxene which adds further evidence to our previous assignment that the luminescence of porous silicon and of the annealed modification of siloxene have the same origin [17,18].

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